Syntheses and Reactions of Polystyrene Derivatives Containing Trivalent Iodine

Syntheses and Reactions of Polystyrene Derivatives Containing Trivalent Iodine

Makoto Okawara*, Yasuhiko Kurusu* and Eiji Imoto*

Starting from poly(p-iodostyrene), several derivatives bearing —I(OAc)$_2$[PJA], —ICl$_2$[PJC], —IO, —IO$_2$ and —I(OBz)$_2$ groups on phenyl nuclei of polystyrene were prepared. The structure and composition of each polymer were deduced by the elementary analysis, iodometry and infrared absorption measurement. All of these derivatives were polymeric oxidizing agents to be useful, for example, as cathodic materials in the electric cell. Particularly, PJA and PJC were effective in the oxidation and chlorination of various organic substances respectively, and, even a selectivity was observed in some cases. Furthermore, the kinetics of the oxidative cleavages of several diols with PJA and with corresponding model compounds were examined to indicate existence of enhanced reactivity and neighboring effect in polymeric system.

1. Introduction

In this laboratory, we have continued the research about the chemical reactions on simple polymeric substances such as polystyrene and polyvinyl alcohol to produce reactive polymers of various types. Some of these reactive polymers have sulfuhydryl,[1] N-halogeno,[2] dihydropyridyl[3] or ferrocenyl[4] group in or along the main chain, and were new kinds of "polymeric oxidizing-" or "polymeric reducing agent" which were superior in some respects to the low molecular weight substances. This investigation was undertaken to establish the synthetic method and characterize the properties of new polystyrene derivatives containing trivalent iodine. Polystyrene (PS) was iodinated first to obtain poly (p-iodostyrene) and, using the latter as a starting material, synthetic methods of PS containing —I(OCOCH$_3$)$_2$, —ICl$_2$, —IO, —IO$_2$, —I(OCOC$_6$H$_5$)$_2$ and —I(SCN)$_2$ groups were examined. The structure and composition of each polymer were deduced by the elementary analysis, iodometric titration and infrared absorption mesurement. These PS derivatives, like the model compounds of low molecular weight, reacted as oxidizing agents and, in particular, the oxidation with PS–I(OAc)$_2$ and the chlorination with PS–ICl$_2$ were found to be useful in organic syntheses. Discharge voltage and capacity were also measured for the electric cell in which the polymeric oxidizing agent was coupled as a cathodic material with magnesium anode. Furthermore, as an example to compare the reactivity of the polymer with that of low molecular weight compound, the kinetics of glycol cleavage with PS–I(OAc)$_2$ and with corresponding model substances were investigated and the neighboring group effect, accelerating or retarding, was observed in some cases for polymeric system.

Experimental details were reported in other papers.[5), 6), 7)]

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2. The syntheses of polystyrene derivatives

The synthetic routes and abbreviations of polystyrene derivatives studied were shown in Fig. 1.
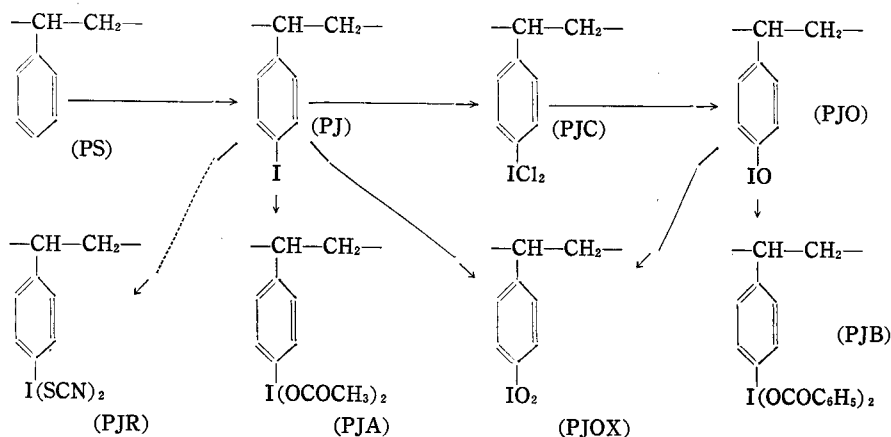

Fig. 1

PS ⟶ PJ

Various kinds of PS which were different in the degree of polymerization and of cross-linking (with divinylbenzene) were used in our study to obtain PJ by iodination with I_2-I_2O_5-H_2SO_4 system. The homogeneous reaction was carried out in nitrobenzene to give PJ with maximum degree of reaction, 86.2%. The iodine content of the polymer was attained to the maximum within 25 hrs. at 95°, but increased not of great since then. In the case of PS of low molecular weight, the iodine content was lower than expected and the isolation of the product was rather troublesome. Cross-linked PS was swelled previously to obtain the maximum iodine content, 59.9%. The results were summarized in Table 1.

PJ ⟶ PJA

Phenyl iodosoacetate, C_6H_5-$I(OAc)_2$ (BJA) was prepared in a high yield by the oxidation of iodobenzene with peracetic acid according to the Pausacker's recipe.[8] Similarly, PJ was added to the 20—25 times (vol.) of 5% peracetic acid and the suspension was stirred for 1-2 hrs. at room temperature and allowed to stand overnight during which the polymer was almost dissolved (standard method). The filtrate was poured into ether to precipitate a white powdery PJA. Iodometry and iodine analysis indicated that the reaction of PJ to PJA proceeded almost quantitatively. Satisfactory results were obtained neither by the mixing acetic anhydride, hydrogen peroxide and PJ in the same time to produce peracetic acid *in situ* (direct method) nor by repeating the standard method twice. The formation of cross-linked PJA failed by all the methods described above. Contrary to PJ, iodobenzene (BJ) dissolved first in the medium and BJA formed was precipitated by the concentration of the solution. The results were shown in Table 2.

Table 1 Iodination of PS

PS kind[a] g. (mM)	$C_6H_5NO_2$ ml.	I_2 mM.	I_2O_5 mM.	CCl_4 ml.	H_2SO_4[b] ml.	time hrs.	yield g	I %	degree of reaction, %	symbol of polymer
P(high) 10.0(96)	250	40	9	10	20	10	15	12.93	23.5	PJ1
// 62.4(600)	1200	240	67	60	120	28	105	46.80	84.9	PJ2
// 20.8(200)	400	80	24	20	40	33	26	45.40	82.3	PJ3
// 31.2(300)	700	120	36	30	60	22	57	47.54	86.2	PJ4
// 5.2(50)	150	20	6	5	10	31	7	48.16	87.3	PJ5
// 10.4(100)	260	60	12	10	20	38	13.5	44.70	81.2	PJ6
// 5.2(50)	110[c]	20	4ml[d]	—	—	4.5	7	37.37	67.7[e]	PJ7
P (low) 10.4(100)	250	40	12	10	20	34	10	39.56	71.7	PJ8
P 4 5.2(50)	150	20	6	5	10	31	7.5	13.40	24.3	P'J1
// 20.8(200)	250	80	24	20	40	50	30	29.20	59.9	P'J2
// 20.8(200)	200	90	24	20	20	37	29	21.57	39.1	P'J3
P 1/2 5.2(50)	130	30	6	5	10	50	8	22.54	40.9	P'J4

a) P(high); obtained commercially, $[\eta] = 0.816$(benzene, 25°). P(low); synthesized in this laboratory, $[\eta] = 0.112$. P4, P1/2; obtained from Zeorite Co. Ltd., granular PS crosslinked with 4% and 0.5% divinyl benzene respectively.　　　b) 50% sulfuric acid　c) sym-dichloroethane　d) conc. nitric acid　e) Nitration occured partially, but the degree of reaction was calculated assuming only monoiodo substituted- and unsubstituted phenyl nuclei existed.

Table 2 Syntheses of PJA

PJ kind g.	AC_2O ml.	H_2O_2 ml.	method	yield g	iodometry[a]	degree of reaction, %	symbol
PJ4 10	170	45	standard	18	2.42	97.9	PJ4A1
PJ4 5	85	23	direct	5.5	1.89	76.3	PJ4A4
PJ6 3	85	20	standard	3	2.00	92.3	PJ6A1
PJ8 5	85	23	//	5.5	2.05	99.7	PJ8A1
PJ3 5	85	23	//	5	0	0	——
PJ4 1	85	20	//	1	0	0	——
P'J4 2	80	20	repeated	2	0	0	——
BJ 10	62	14	standard	14	3.03	97.7 (purity)	BJA

a) I_2(mM) isolated from KI by the oxidation with 1g. of polymer.

PJA is insoluble in water and in common organic solvents, while it soluble sparingly in acetic acid. In order to examine the stability of PJA(and BJA), the quantitative assay of the sample kept in a sealed vessel was carried out as shown below.

PJ4A1　purity, 78.2%　　after a week, 78.1%

PJ4A2　　//　85.3%　　　//　　83.5%

BJA　　//　97.7%　　　//　　96.4%

PJ ⟶ PJC

Blowing the dry chlorine into a solution of BJ in chloroform, phenyl iodosochloride,

C₆H₅–ICl₂(BJC) was obtained easily as an yellow powder.[9] PJ was converted to PJC in a similar way. PJC thus obtained, however, was a rubbery mass and difficult to purify. The powdery PJC was obtained by means of dropping a solution of PJ into a solution of chlorine in chloroform arranged previously. Blowing method could not perform the chlorination of cross-linked PJ effectively but, steeping P'J in chlorine solution a granular P'JC was produced with comparative ease. The efficiency of the chlorination was high in the polymer of low iodine content such as PJ₁.

PJC was pulverized, washed enough with ether and dried in vacuo for 3 hrs.. The degree of reaction, the ratio of factor found to that calculated based on the iodine content of original PJ was determined by iodometry and shown in Table 3 with the conditions of chlorination.

PJC was insoluble in common solvents and had a chlorine-like odor. On standing, the factor decreased gradually and a few examples of decay curve were indicated in Fig. 2. Though the differences in decreases of factor were not so large among BJC, PJ₂C₁ and

Table 3   Chlorination of PJ

PJ kind	PJ g.	I₂ mg. atom	CHCl₃ ml.	temp. °C	time min.	yield g	iodometry[a]	degree of reaction, %	symbol
PJ₁	6	6.1	300	0—5	60	6	0.242	101.5	PJ₁C
PJ₂	6	22.2	270	5—10	30	6	0.420	57.1	PJ₂C₁
PJ₂	6	22.2	300	0—5	50	7.6	0.607	82.5	PJ₂C₂
PJ₂	6	22.2	300[b]	0—5	120	8	0.396	53.9	PJ₂C₃
PJ₃	2	7.5	250[b]	5—10	30	2.5	0.406	54.6	PJ₃C₁
PJ₃	4	15.0	270	5—10	40	4.5	0.406	54.6	PJ₃C₂
PJ₃	3	11.0	200[c]	0—5	40	3.3	0.697	93.7	PJ₃C₃
PJ₃	10	37.4	300[c]	0—5	40	15.0	0.369	49.7	PJ₃C₄
P'J₃	14	23.7	150	20	24hrs.	25.8	0.148	23.9	P'J₃C
BJ	25	120	40	0—5	60	33	0.923	98 (purity)	BJC

a) I₂(g.) isolated from KI by the oxidation with 1g. of polymer.
b) chloroform which was used in the previous chlorination.
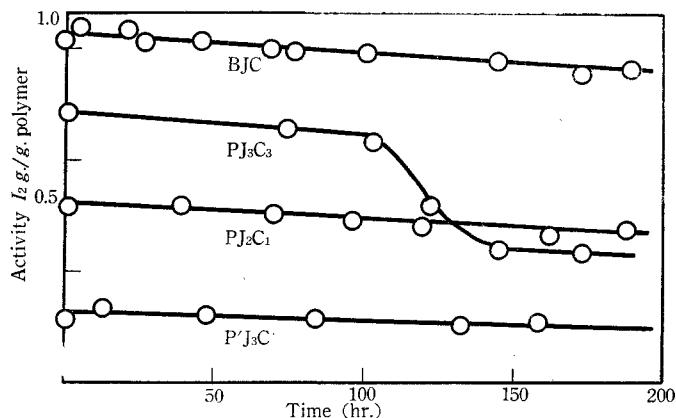c) a chlorine solution in chloroform was used.

Fig. 2   Stability of PJC

P'J$_3$C, PJ$_3$C$_3$ (high chlorine content) decayed considerably in the initial stage and stabilized at around 50% of the reaction. One example of structure was shown in Fig. 3 which was deduced from the content of chlorine in PJC and that of iodine in original PJ. The value of [η] of PJ which was regenerated by the dechlorination of PJ$_2$C$_2$ (prepared six months before) with potassium iodide was 0.275 (benzene, 25°), fairly low compared with 0.435 of original PJ$_2$, and the fact suggested the cleavage along the main chain had occured to some extent in preservation.

PJC $\longrightarrow$ PJO, PJOX

In the usual way,[10] BJC was hydrolyzed to BJO in 83% yield, and the latter was boiled with water to give BJOX. In the case of the polymer, PJO was produced by

PJ$_1$C$_1$

$-(-CH-CH_2-)_{88}-(-CH-CH_2-)_{12}-$

ICl$_2$

factor { obs. 0.242 calc. 0.238

PJ$_2$C$_2$

$-(-CH-CH_2-)_{29}-(-CH-CH_2-)_{15}-(-CH-CH_2-)_{56}$

I   ICl$_2$

factor { obs. 0.607 calc. 0.606

PJ$_3$C$_3$

$-(-CH-CH_2-)_{27}-(-CH-CH_2-)_{6}-(-CH-CH_2-)_{67}$

I   ICl$_2$

factor { obs. 0.697 calc. 0.695

PJO

$-(-CH-CH_2)_{27}-(-CH-CH_2-)_{45}-(-CH-CH_2-)_{28}$

I   IO

factor { obs. 0.355 calc. 0.353

PJOX

$-(-CH-CH_2-)_{x}-(-CH-CH_2-)_{y}-(-CH-CH_2-)_{z}$

I   IO$_2$

	I	II	III	IV
x	27	29	29	29
y	64	36	41	58
z	9	35	30	13
factor { obs.	0.231	0.863	0.748	0.339
calc.	0.229	0.866	0.748	0.333

PJB

$-(-CH-CH_2-)_{27}-(-CH-CH_2-)_{52}-(-CH-CH_2-)_{21}-$

I   I(OCOC$_6$H$_5$)$_2$

factor { obs. 0.219 calc. 0.222

PJR

$-(-CH-CH_2-)_{27}-(-CH-CH_2-)_{70}-(-CH-CH_2-)_{3}$

I   I(SCN)$_2$
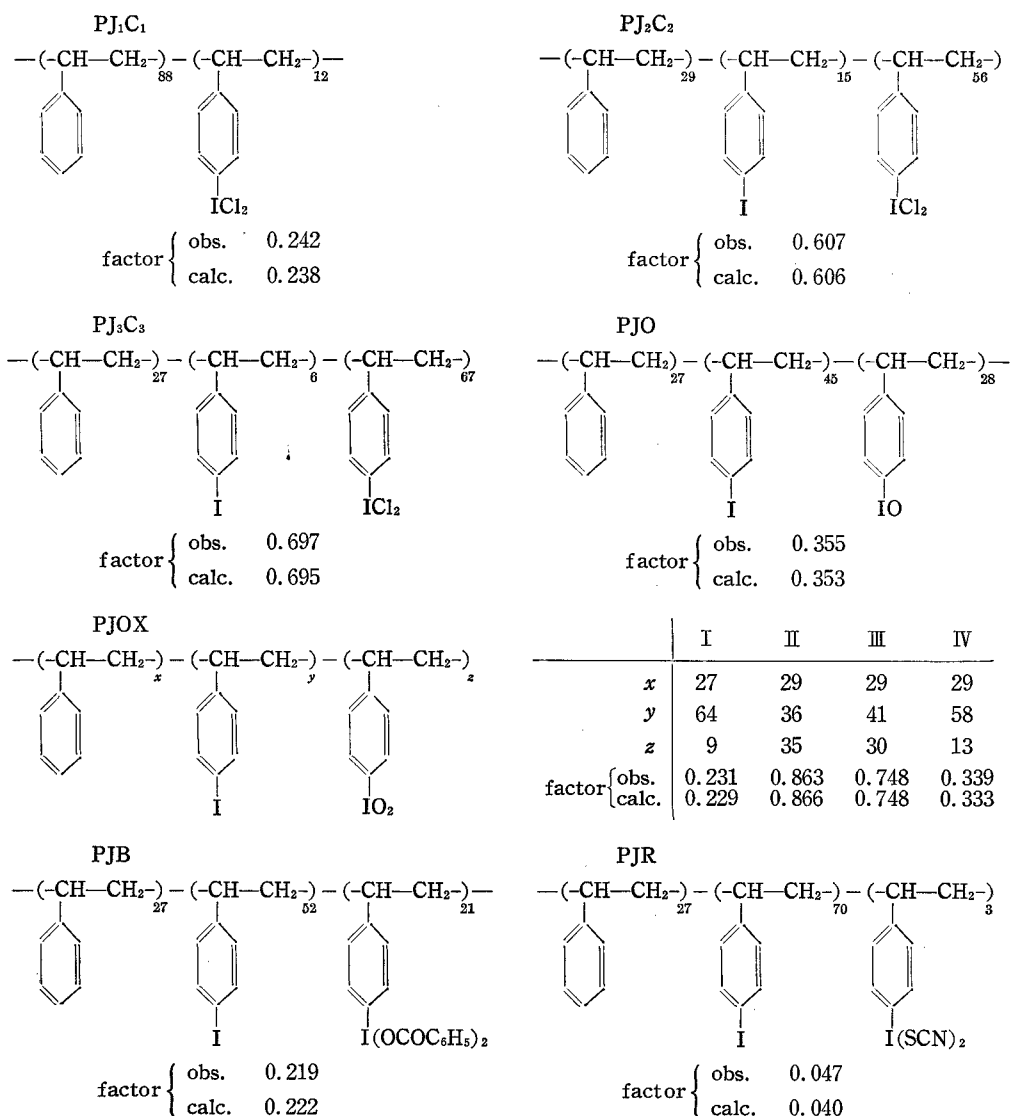
factor { obs. 0.047 calc. 0.040

Fig. 3 Structure of PJ derivatives

kneading well PJC with aqueous sodium carbonate and letting alone. The structure of PJO was estimated as PJO in Fig. 3 based on the factor obtained by iodometry, assuming the chlorine reacted perfectly. PJOX was obtained by boiling PJO with water for 18 hrs. and the structure was estimated as PJOX-1 in Fig. 3 in the same way. The structure was further rationalized by the reactivity and infrared spectrum as discussed later.

PJ ⟶ PJOX

BJOX was also obtainable by the oxidation of BJ with Caro's acid[11] or perbenzoic acid.[12] PJOX was produced by treating 1 g. of PJ with $K_2S_2O_8$ (30 g.) and conc. sulfuric acid (20 g.) below 60° as an yellow-brown powder. The structure based on iobometry was as PJOX-II in Fig. 3. Similarly, another PJOX was prepared as a white powder by adding a chloroform solution of PJ (2 g.) into a same solution of perbenzoic acid (5.39 mM) followed by standing overnignt and pouring in petroleum ether. While the structure of such a polymer was seemingly to be as PJOX-III in Fig. 3, it should be contaminated with carbonyl group which was detectable by infrared spectrum measurement as described later. Furthermore, as PJOX-III gave some benzoic acid by hydrolysis with 1N-HCl, it may contain partially a benzoate unit in the structure.

The formation of BJOX was also observed by the oxidation of BJ with monoperphthalic acid (PPA). When 1 g. of PJ was dissolved in dioxane and added to a dioxane solution of PPA (1.5 mM.), the gelation occured within 2 hrs.. After 12 hrs., the mixture was thrown in petroleum ether and factor of a pale yellow polymer thus obtained was determined by iodometry to give the structure such as PJOX-IV in Fig. 3. Even in the case, the polymer may contain the phthalate type unit in part such as (I), (II), considering from the results of infrared spectrum, acidic hydrolysis and iodine analysis.

(I)   (II)
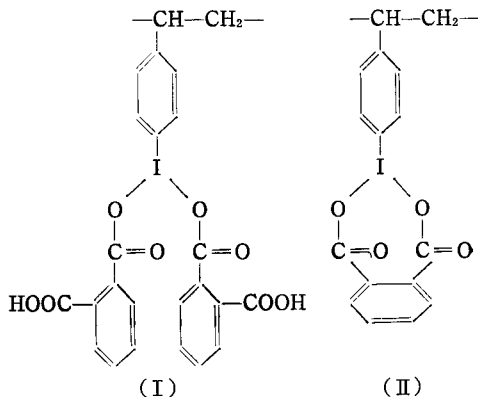
PJO ⟶ PJB

While PJA was easily obtained by the reaction of PJ with peracetic acid, PJOX type polymer, instead of PJB, was produced predominantly by the reaction of PJ with perbenzoic acid. So, according to the fact[13] that BJB is synthesized by the reaction of BJO with benzoic acid in the yield of 81%, the synthesis of PJB through PJO was undertaken. PJO was added to a solution of benzoic acid in chloroform and the solution being shaked for 30 hrs., a white powdery polymer was obtained. The structure deduced from the factor was shown in Fig. 3. If, as described above, ester type compounds are produced by the reaction of iodoso group with carboxyl group, the polymer shown in following equation might be obtained by the reaction of BJO with polyacrylic acid. BJA and methanol were added to an aqueous solution (20%) of polyacrylic acid and the solution, allowed to

$$-(-CH-CH_2-)- \quad + \quad C_6H_5IO \quad \longrightarrow \quad (-CH-CH_2-)- \; - \; -(-CH-CH_2-CH-CH_2-)-$$
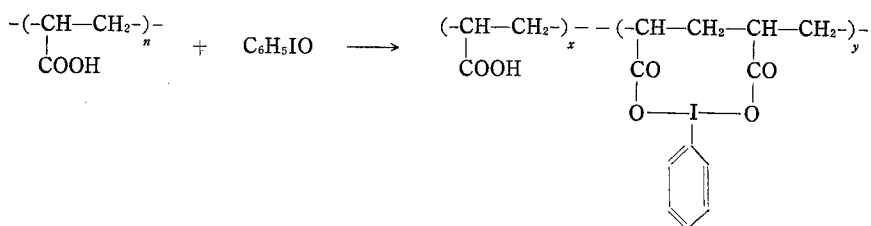
stand overnight after shaking for 3 hrs. at room temperature, was filtered, washed with water and dried in vacuo. The polymer obtained was a white powder, and insoluble in alcohol, acetic acid, dimethylformamide and dioxane, but gradually swelled in water. The factor and iodine content calculated from above equation ($x=84$, $y=16$) were 0.344 and 19.98% respectively, and those observed were 0.351 and 17.52%. The stretching vibration (KBr) of the polymer at 1710-20, 1320 and 1270 cm^{-1} was assigned to C=O and the fact allowed to assume the presence of ester type in the structure, while a small amount of BJO unit might remain physically.

Infrared spectra of the polymers

Because of the insolubilities of the polymers prepared above in ordinary organic solvents, all the measurements of spectra were carried out by KBr method. The absorption band of PJA at 812 cm^{-1} might be assigned to the C-H stretching vibration of para-substitution and the band was not observed in PS. The stretching vibration for C-O was observed around 1260-1280 cm^{-1} and for C=O at 1640 cm^{-1} in PJA. The corresponding frequencies of C-O stretching of BJA were at 1263 and 1285 cm^{-1}, while the band assigned to C=O stretching was shifted to 1625 and 1643 cm^{-1} due to the positive field effect of iodine atom as shown by formula (III). Furlani[14] and Bell[15] used the bands, 745 cm^{-1} in BJO, and 710, 770 cm^{-1} in BJOX as key bands in their reports. While the absorption at 745 cm^{-1} was found in our BJO, it disappeared gradually in three days and instead a strong band at 770 cm^{-1} and a weak band at 710 cm^{-1} appeared probably due to the disproportionation. The presence of –IO$_2$ group in our BJOX was shown by the strong absorption at 772 and 710 cm^{-1}, but the corresponding absorption for PJO and PJOX-I were considerably broad. While the absorption of PJOX-II was similar to that of PJOX-I, the new bands at 1645-50, 1317, 1285 and 1175 cm^{-1} were detected in addition to 760 and 712 cm^{-1} in PJOX-III. On the other hand, the band at 745 cm^{-1} (–IO) disappeared and the strong absorption at 1658, 1617, 1325, 1273 and 1174 cm^{-1} (C=O and C-O of benzoate) were found in BJB prepared from BJO and benzoic acid. Consequently, the partial formation of –I(OCOC$_6$H$_5$)$_2$ was deduced in the reaction of PJ with perbenzoic acid and the fact was supported by the presence of absorption at 1600-1700 cm^{-1} (assigned to C=O stretching of phthalate) in PJOX-IV made from PJ and monoperphthalic acid. When PJO was allowed to react with benzoic acid in chloroform, PJB was produced, which showed the bands at 765 and 710 cm^{-1} (–IO$_2$) and the fact indicated the disproportionation of –IO to –IO$_2$ had occured in part.
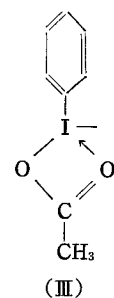
The reaction of PJ with thiocyanogen

Neu[16] reported that aniline was easily thiocyanized with BJC in the presence of metal thiocyanate and Wood[17] assumed the intermediate, $C_6H_5I(SCN)_2$, as an active species of thiocyanation. Then, we may expect the formation of polymeric PJR from the reaction of PJC with lead thiocyanate. However, due to the insolubility of lead thiocyanate and PJC in the same solvent, the reaction of thiocyanogen with PJ was examined in the homogeneous state. A solution of PJ (I: 1.1×10^{-2} g. atom) in chloroform was added to a solution of thiocyanogen (1.51×10^{-2} M) in the same solvent and the homogeneous mixture was poured into petroleum ether after 6 hrs.. The factor (iodometry) of a pale orange polymer thus obtained was low and the structure might be as PJR in Fig. 3 if it existed. Any increase of factor was not observed by using two to four times of thiocyanogen. The situation was the same by adding PJ in solid state or by using carbon tetrachloride in place of chloroform. Alternatively, UV spectra were measured for BJ, PJ, BJ-(SCN)$_2$ and PJ-(SCN)$_2$ system in chloroform and the result was shown in Fig. 4. From the figure, it may be obvious that the absorption intensity of BJ-(SCN)$_2$ and PJ-(SCN)$_2$ system was almost equal to the sum of intensity of each component respectively, and, new absorption, then, any interaction of thiocyanogen with BJ or PJ did not exist. Consequently, the thiocyanation might be performed either by thiocyanogen itself due to the right shift of equilibrium in the equation,

Fig. 4 Spctra of BJ, PJ, (SCN)$_2$

A: BJ 4.25 mM/l
B: (SCN)$_2$ 3.86 mM/l
C: BJ+(SCN)$_2$ each conc. is equal to A, B respectively
D: Calculated curve from A, B
E: PJ$_3$ 20.1 mM/l
F: (SCN)$_2$ 18.2 mM/l
G: PJ$_3$+(SCN)$_2$ each conc. is equal to E, F respectively
H: Calculated curve from E, F

$$\begin{array}{c} C_6H_5ICl_2 \\ Pb(SCN)_2 \end{array} \longrightarrow \begin{array}{c} PbCl_2 \\ C_6H_5I(SCN)_2 \end{array} \underset{\longleftarrow}{\xrightarrow{\hspace{2cm}}} C_6H_5I + (SCN)_2$$

or by chlorthiocyan produced in the following equation described by Bacon.[18]

$$C_6H_5ICl_2 + Pb(SCN)_2 \longrightarrow C_6H_5I + PbCl_2 + 2Cl\text{-}SCN$$
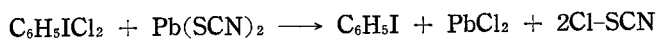
3. Reactions of polystyrene containing trivalent iodine

All of PJA, PJC and PJO obtained above are oxidizing agents capable of liberating iodine from potassium iodide. When the proper oxidation reactions are performed by these polymeric reagents, the polymer reduced to PJ type is removed easily from the system
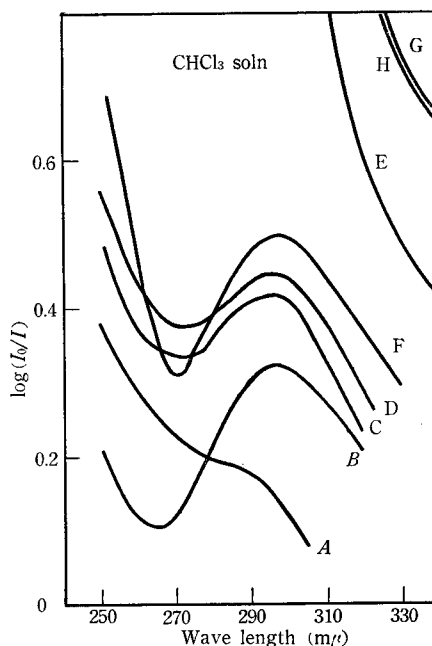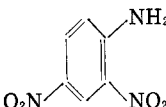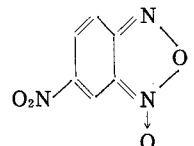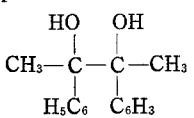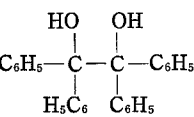
after oxidation and the PJ should be regenerated in the form of PJA, PJC and so on to be used repeatedly. By the way, if a specific effect is ensued due to the polymeric structure of the reagent, a selective oxidation may be possible which is not expectable in the model compound of low molecular weight. In this respect, the following several reactions were investigated.

Oxidation with PJA

The results were summarized in Table 4. For example, to a suspension of 2.0g. (0.01 mole equivalent) of PJA in 80 ml. of benzene, added a benzene solution (2 mole/1) containing 0.46 g. (0.005 mole) of aniline. The solution began immediately to discolor accompanying with heat and turned to brown-black after ten minutes. After standing for 24 hrs., resulted homogeneous reaction mixture was concentrated and followed by chromatography on alumina to give 330 mg. of azobenzene as a yellow-red crystal, mp. 66-67°. A pale brown precipitate, obtained by pouring a reaction mixture into methanol, was dissolved in benzene and reprecipitated with methanol to recover PJ in 90% yield.

Table 4   Oxidation with PJA

| reactant compound	mM.	reagent polymer	mM.	solvent	temp. °C	time hrs.	product	yield %
$C_6H_5NH_2$	5	PJ_4A_1	5	C_6H_6	25	24	$C_6H_5-N=N-C_6H_5$	73
O_2N—⟨NH_2, NO_2 ring⟩	5	PJ_4A_1	7.5	C_6H_6	80	2	(benzofurazan N-oxide structure)	35
p-MeC_6H_4NHAc	5	PJ_4A_2	7.5	AcOH	25	72	p-Me m-AcOC_6H_3NHAc	51
$CH_3-\underset{H_5C_6}{\overset{HO}{C}}-\underset{C_6H_3}{\overset{OH}{C}}-CH_3$	3.3	PJ_4A_1	5	C_6H_6	80	3	$C_6H_5COCH_3$	43
$C_6H_5-\underset{H_5C_6}{\overset{HO}{C}}-\underset{C_6H_5}{\overset{OH}{C}}-C_6H_5$	3.3	PJ_4A_1	5	C_6H_6	80	8	$C_6H_5COC_6H_5$	26

Chlorination with PJC

PJC was mixed with an equivalent of reactant in chloroform and allowed to stand after shaking. Initially suspended PJC turned to PJ and dissolved as the reaction proceeded. After standing for a definite time, the product was separated in the proper manner. The results were shown in Table 5.

PJ was recovered almost completely in each case. The efficiency of nuclear chlorination was not so excellent, but, a selectivity was observed in the case of salicylic acid in which the substitution occured on the 5-position predominantly. Selectivity was also shown in the chlorination of double bond as the preferred formation of *meso*-dichloride in the case of cis-stilbene indicated the cis addition of chlorine had occured. Various mechanism are proposed for the chlorination with BJC and only one example of cis addition was reported

Table 5   Chlorination with PJC
(in chloroform at room temp.)

reactant compound	mM.	reagent polymer	mM.	time hrs.	product	mp. (lit.)	yield %
C_6H_5NHAc	5.1	PJ_2C_1	3.3	24	p-ClC_6H_4NHAc	174(174)	45.5
p-HO—C_6H_4COOH	5.2	PJ_2C_1	3.3	24	5-Cl, 2-OHC_6H_3COOH	172(173)	56.8
$C_6H_5CH=CHCOC_6H_5$	8.2	PJ_1C_2	14.3	24	$C_6H_5CHClCHClCOC_6H_5$	113(113)	87.6
$C_6H_5CH=CHC_6H_5$							
cis-	5.5	PJ_3C_4	5.5	24	$meso(C_6H_5CHCl)_2-$	190(190)	55.7
trans-	5.5	PJ_1C	4.8	48	〃	〃 〃	57.5
acenaphthylene	6.5	PJ_3C_4	6.7	24	cis 1,2-dichlor- acenaphthene	116(116)	33.5

by Barton[19] in the case of coresterol. The formation of intermediate such as (IV) (cis addition) may be advantageous on the solid surface of insoluble polymer. It is interesting the cis addition of chlorine in acenaphthylene-PJC system is the reverse of the case (trans addition) of BJC reported by Cristol.[20]

$$>C \text{====} C<$$

with Cl and Cl bridged by I (IV)
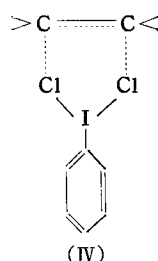
Oxidizing abilities of iodoso- and iodoxy compounds

BJOX is soluble slightly in water, dimethylformamide and dimethylsulfoxide but BJO, PJO and PJOX are not in all the solvents tested. Therefore, the oxidizing abilities of these polymers were examined qualitatively as summarized in Table 6. Iodoso- or iodoxy compounds ars added in solid form to the dilute solution of each reactant and the discoloration was observed after shaking for 5—10 minutes. The general conclusion is derived from the table that the oxidizing power of iodoxy compound is weak comparing with iodoso compound and difference between polymer and model compound of low molecular weight is not so distinct.

Table 6   Oxidizing abilities of PJO and PJOX

reactant	solvent	BJO	PJO	BJOX	PJOX
KI	dil. H_2SO_4	←———————	liberate I_2	————————————	——→
methyleneblue	H_2O	←———————	not discolor	————————————	——→
neutralred	C_2H_5OH/H_2O	decolor	decolor	not discolor	not discolor
thionine		decolor	decolor	not discolor	not discolor
hydrazine	10% aq.	←———————	liberate N_2	————————————	——→
hydrazobenzene	C_2H_5OH	russet	orange	unchange	unchange
hydroquinone	H_2O	black-brown	yellow-brown	unchange	unchange
aniline	C_2H_5OH	black-brown	black-brown	unchange	unchange

Cell reaction[21]

Because of the insolubilities of the reagents (including polymers and corresponding model compounds), it is difficult to measure their redox potentials exactly. Then, the discharge potentials of the cell were measured using the oxidizing agent as a cathodic material and magnesium plate as an anode by the partially modified apparatus of Glicksman.[33]

A carbon rod cathode, inserted in a kneaded mixture of 0.5 g. of compound and 0.05 g.

of acetylene black, was combined with a magnesium plate in magnesium bromide electrolyte (11.8% aq.). The relation of potential (*vs.* S.C.E.) to time at the constant current discharge (30 mA/g.) was plotted in Fig. 5 together with the results of the model compounds of low molecular weight as comparison. Table 7 shows the capacity as the product of current by time required to drop 0.5 volt from the initial voltage.
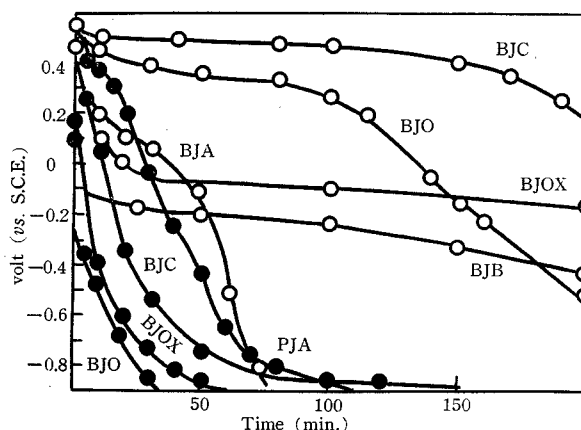

Fig. 5 Cathode electrode potentials of the compunds containing trivalent iodine.

Table 7 Capacites of the compounds containing trivalent iodine

| compound | iodometry[a] | | capacity |
	calc.	obs.	(amp. min./g.)
BJA	6.189×10^{-3}	6.187×10^{-3}	1.20
BJC	7.275×10^{-3}	6.751×10^{-3}	6.39
BJO	9.085×10^{-3}	6.104×10^{-3}	3.85
BJOX	16.9×10^{-3}	15.36×10^{-3}	5.55
BJB	5.189×10^{-3}	4.880×10^{-3}	0.75
PJA	5.73×10^{-3}	1.43×10^{-3}	3.24
PJC	6.59×10^{-3}	3.53×10^{-3}	0.69
PJO	8.08×10^{-3}	2.27×10^{-3}	0.75
PJOX	15.2×10^{-3}	1.66×10^{-3}	1.22

a) calculated and observed I (g.atom) isolated from KI by the oxidation with 1 g. of polymer

4. Kinetics of the reactions of PJA and its model compounds with 1, 2-diols

Method and result

As cited above, PJA cleaves 1,2-diols to yield carbonyl compounds. Here, we studied the kinetics of reactions of PJA and its three model compounds with four 1,2-diols shown in Table 8. Of all model compounds, CJA (mp. 94-95°) was obtained by the oxidation of p-iodocumene with peracetic acid in the same manner as BJA and the structure was confirmed by the elementary analysis, iodometric titration and infrared spectrum. DJA

(mp. 61–63°) was obtained by the oxidation of 1,3-di(p-iodophenyl)-propane (mp. 80–81°) which was in turn produced from 1-3-diphenyl propane by means of I_2–I_2O_5 method. The purity of DJA obtained here was 95.8% (iodometry).

The reaction was carried out in acetic acid at 55–65°. Initial concentrations of PJA or its model compounds (a) and diols (b) were $2-4\times10^{-3}$ mole/1 respectively. Each solution attained to the constant temperature in the thermostatt was mixed and the course of oxidation was followed by periodically removing a 5 ml. portion adding to acidified potassium iodide, and titrating the liberated iodine with N/100 sodium thiosulfate. Plotting $2.303/(a-b)[\log b(a-x)/a(b-x)]$ against t, a straight line was obtained as shown in Fig. 6. Calculating the slope by the method of least squares, second-order rate constant k $(1, \text{mole}^{-1}, \text{sec.}^{-1})$ was obtained. Temperature and $\log k$ obey the Arrhenius equation as illustrated in Fig. 7 and the values of E and $\log A$ calculated for various JA-diol system were summarized in Table 8 together with the value of k.
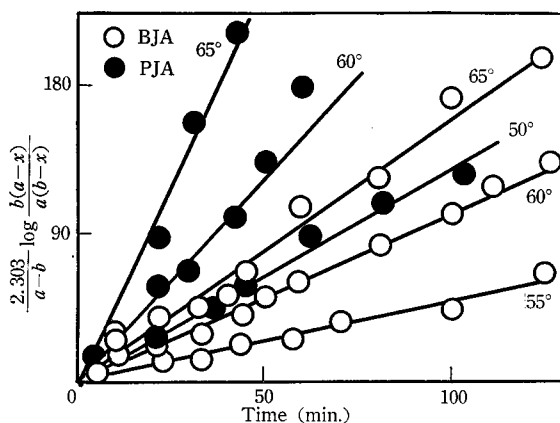
Fig. 6   Reactions of *meso*-hydrobenzoin (B₁) with BJA and PJA (CH₃COOH).
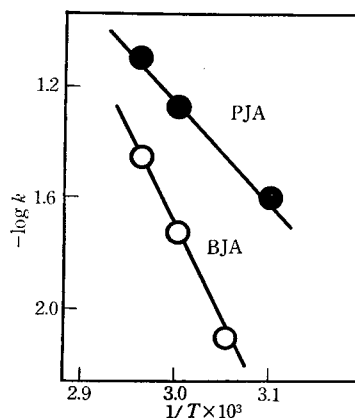
Fig. 7   Relations between $-\log k$ and $1/T$ for the reactions of *meso*-hydrobenzoin (B₁) with BJA and PJA.

Discussion

From the results of Table 8, it is difficult to find a definite regurality for the values of E and $\log A$ which are variable considerably depending on the kinds of JA and diols. There is, however, a linear relationship between the values of E and $\log A$ as indicating in Fig. 8 for BJA and PJA.

Pausacker[23] investigated the effect of composition of solvent on the rate of the reaction of BJA with benzopinacol at 16–60°. In the case, using the mixed solvent (acetic acid-benzene), the value of E varied from 10.96 to 23.70 Kcal/mole and $\log A$, from 5.76 to
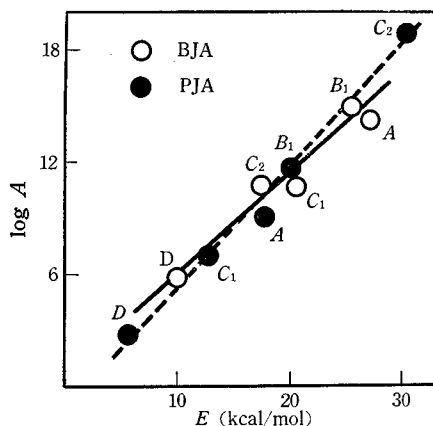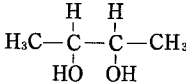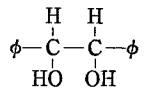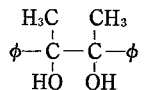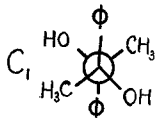
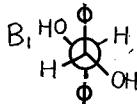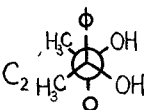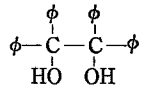

Fig. 8   Relations between E and $\log A$ for the reactions of 1,2-diols with PJA and BJA.

Table 8 Reaction of JA with 1,2-diol

diols \ JA		BJA — I(OAc)₂ $(t°C)\ k\times10^3$	E (log$A$)	CJA (H₃C—CH—CH₃) — I(OAc)₂ $(t°C)\ k\times10^3$	E (log$A$)	DJA (CH₂—CH₂—CH₂) — I(OAc)₂ I(OAc)₂ $(t°C)\ k\times10^3$	E (log$A$)	PJA (—CH—CH₂—) — I(OAc)₂ $(t°C)\ k\times10^3$	E (log$A$)
H₃C—C(H)(HO)—C(H)(OH)—CH₃	A	(55) 0.35 (60) 0.44 (65) 1.09	25.1 (14.1)	(60) 0.41				(55) 3.06 (60) 4.38 (65) 6.66	17.3 (9.16)
φ—C(H)(HO)—C(H)(OH)—φ	B₁ (meso)	(55) 8.77 (60) 16.9 (65) 27.1	24.7 (14.4)	(50) 5.7 (60) 11.7 (65) 26.1	23.0 (16.9)			(50) 23.6 (60) 54.7 (65) 80.9	19.4 (11.5)
	B₂ (dl)	(60) 17.2 (65) 26.6						(60) 15.9	
H₃C, CH₃ φ—C—C—φ (HO OH)	C₁ (meso)	(55) 6.45 (60) 10.2 (65) 15.6	19.4 (10.8)					(55) 22.3 (60) 29.5 (65) 39.6	12.6 (7.46)
	C₂ (dl)	(55) 9.2 (60) 20.9 (65) 30.2	17.6 (9.8)	(50) 12.9 (60) 44.0 (65) 78.0	25.2 (15.3)	(55) 19.9		(50) 12.9 (60) 43.0 (65) 88.1	29.9 (18.4)
φ—C(φ)(HO)—C(φ)(OH)—φ	D	(50) 9.85 (60) 15.7 (65) 18.9	10.3 (5.3)	(35) 3.6 (43) 5.7 (50) 19.9	23.4 (14.0)	(55) 4.61 (60) 8.36 (65) 14.8	25.7 (14.8)	(50) 20.8 (60) 23.5 (65) 30.8	5.62 (2.15)

14.09 depending on the composition of the solvent, and, the linear relationship was found between enthalpy, ΔH, and entropy, ΔS, of activation. The Leffler's "isokinetic relationship",[24]

$$\Delta H = \Delta H_0 + \beta \Delta S$$

is expressed in that case as following,

$$\Delta H = 21.59 + 320.8 \, \Delta S$$

and, the isokinetic temperature (the temperature at which all reactions obeying the same isokinetic relationship will proceed at the same rate) is 48°. In such a case, it is impossible to compare strictly the relation between the rate and composition of solvent at the temperature range of 16-66°. Rather low values of β, 60° or 95°, is reported[23],[25] in the similar reaction of 1,2-diols with leadtetraacetate. Therefore, the temperature range of 50-65° used in our experiments seems to be closed to the value of β and it may be meaningless to discuss exactly the relation of the rate to the structure of the compounds. The cyclic intermediate which had been hitherto postulated for the mechanism of the oxidative cleavage of 1,2-diols with leadtetraacetate or periodic acid explains the fact that the cis-diols are cloven more easily than the trans in general. However, the radical mechanism is proposed in the case of trans-decalin-9,10-diol as well as the hydrogen bond mechanism[26] in another case. Furthermore, some reversed examples are found recently in which the cis-diol is not always oxidized more easily than the trans.[27] Together with the above results, the fact that comparisons in the literatures were almost tried on the value of k at any temperature, but not on E and $\log A$, makes it impossible to compare our results with the conclusion derived from the results obtained up to date. However, dividing the diols used here in two parts, one having α-H in regard to OH (A, B) and the other not (C, D), following tendencies may be observed.

1. For a definite JA, large differences are not observed in the value of E and $\log A$ of compounds A and B.

2. For a definite JA, the values of E and $\log A$ of D are smaller than those of C respectively.

3. Concerning the reactions of low molecular weight JA with D, the larger the molecular size of JA, the more the values of E and $\log A$ increase.

4. In many cases, PJA is more reactive (decrease in E) than low molecular weight JA and the tendency attains maximum in the case of D.

5. dl-form is more reactive than meso-form, agreed with the general tendency, cis>trans, except in the reaction of dl-C (C_2) with PJA in which extraordinary large value of E and $\log A$ is observed.

Exact explanation of these all results is impossible. However, we suppose that the polymeric PJA reacts more easily, contrary to our expectations, than low molecular weight model compounds as following. The rate of reaction of PJA with diols deviates from exact second order kinetics and decreases as the reaction proceeds below 60°. Against the another OH radical of the diol bound to the polymer through O-I linkage, neighboring acetate radical attacks nucleophillically to facilitate the cleavage of H-O, C-C and I-O

bonds successively as shown below (V). This accelerating effect should decrease as the reaction proceeds to reduce the number of neighboring acetate radical. As such an effect should be complicated by the spacial configuration of intermediate, and then, structures of diols themselves, apparent random of the results may be inevitable. In the reaction of PJA with benzopinacol at 70° under the similar condition (initial rate constant $k=3.0\times$

(V)   (VI)
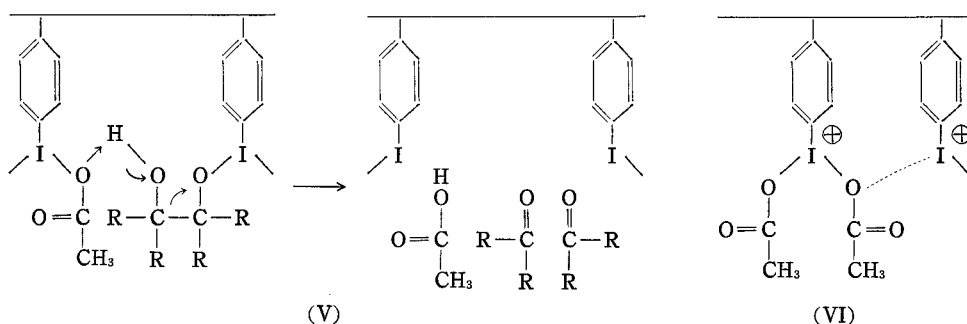
10^{-2} 1, mole^{-1}, sec.$^{-1}$), the rate of decrease of PJA deviates from second order straight line after 80 minutes and increases progressively as the reaction proceeds. The fact may be explained as a result that the positive electric field of iodine atom on $-C_6H_5I$ produced attacks the neighbored I-OAc radical to weaken the I-O bond as shown in above (VI). This consideration may be consisted with the result of Leffler in which the o-iodo substituted benzoyl peroxide decomposes in chloroform several thousands times faster than non-substituted benzoyl peroxide.[28] Sorption of reagent on polymeric molecule which is sometimes observed in the polymer reaction may be correlated to the result, but the further conclusion will be erroneous at present.

References

1) M. Okawara et al., *Kogyo Kagaku Zasshi*, **60**, 73 (1957), **61**, 1508 (1958), **64**, 226, 229 (1961).
2) M. Okawara et al., *Kogyo Kagaku Zasshi* **60**, 75 (1957), **65** 819, 1658 (1962).
3) M. Okawara, T. Sasaoka, E. Imoto, *Kogyo Kagaku Zasshi* **65**, 1652 (1962).
4) M. Okawara et al., *Kogyō Kagaku Zasshi* **65**, 685 (1962).
5) M. Okawara, K. Mizuta, *Kogyo Kagaku Zasshi* **64**, 232 (1961).
6) M. Okawara, Y. Kurusu, E. Imoto, *Kogyo Kagaku Zasshi* **65**, 816 (1962).
7) M. Okawara, Y. Kurusu, E. Imoto, *Kogyo Kagaku Zasshi* **65**, 1647 (1962).
8) K. H. Pausacker, *J. Chem. Soc.* **1953**, 107.
9) *Org. Synth.* Col. Vol. III p. 482 (1955).
10) *Org. Synth.* Col. Vol. III p. 483 (1955).
11) E. Bamberger, A. Hill, *Ber.* **33**, 533 (1900).
12) B. A. Arbusow, *J. Prakt. Chem.* **131**, 357 (1931).
13) D. H. Hey, C. J. Stirling, G. H. Williams, *J. Chem. Soc.* **1956**, 1475.
14) C. Furlani, G. Sartori *Ann. Chim. (Rome)* **47**, 124 (1957): *Chem. Abst.* **51**, 8533 (1957).
15) R. Bell, K J. Morgan, *J. Chem. Soc.* **1960**, 1209.
16) R. Neu, *Ber.* **72**, 1505 (1939).
17) J. L. Wood, *Organic Reactions* vol. 3 (1946) p. 255.
18) R. G. R. Bacon, R. G. Guy, *J. Chem. Soc.* **1960**, 318.
19) D. H. Barton, E. Miler, *J. Am. Chem. Soc.* **72**, 370 (1950).
20) S. J. Cristol, F. R. Stermitz, *J. Am. Chem. Soc.* **78**, 4939 (1956).
21) M. Okawara et al., to be published.

22) R. Glicksman, C. K. Morehouse, *J. Electrochem, Soc.* **103,** 94 (1956).

23) K. H. Pausacker, L. K. Dyall, *J. Chem. Soc.* **1958,** 3950.

24) J. E. Leffler, *J. Org. Chem.* **20,** 1202 (1955).

25) J. P. Corduer, K. H. Pausacker, *J. Chem. Soc.* **1953,** 102.

26) M. S. Newman, "Steric effects in organic chemistry" (1956) p. 378 John Wiley and Sons Inc.

27) P. Levesley, W. Waters, A. N. Wright, *J. Chem. Soc.* **1956,** 846.

28) J. E. Leffler et al., *J. Am. Chem. Soc.* **80,** 5435 (1958).