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Preparation of Star-Type Graft Copolymer through the Polymerization of Methyl Methacrylate with Use of the Potassium Complexes of Polystyrene having a Benzophenone Unit

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Polystyrene ketone possessing a benzophenone structural unit in the middle part of the chain was synthesized by the coupling reaction of one-ended living polystyrene with 2,4′-dichlorobenzophenone. Polystyrene ketone potassium ketyl was prepared by the reaction of polystyrene ketone with an equivalent amount of potassium naphthalene complex in tetrahydrofuran. Polystyrene ketone potassium dianion was also formed with excess potassium in the solvent. These polystyrene ketone potassium adducts induced a quantitative polymerization of metyl methacrylate. Gross polymer from each of the reaction systems was elution-fractionated into four fractions in which a new class of star-type graft copolymer was included together with polystyrene and polymethyl methacrylate. Each fraction was characterized by means of the measurements of the yield, molecular weight and styrene content. Consideration was also made on a possible mechanism of the polymerization.

Syntheses of well defined block, graft and star-type branched copolymers by means of anionic living polymerization have been recently developed.[1-11] Polymerization and graft copolymerization initiated by the alkali metal complexes of aromatic ketone and of polyvinyl benzophenone have also been studied.[12-17] An attempt was made in a previous paper[18] to prepare a new class of star-type graft copolymers with different kinds of branches, starting from the potassium adducts of polystyrene ketone possessing one or two carbonyl groups in the middle part of the chain. Few investigations, however, have been made as to the mechanism of initiation by ketyl or dialkali metal complexes. The present paper is concerned with an attempt to obtain star-type graft copolymers with polymethyl methacrylate branches, starting from the potassium adducts of polystyrene ketone possessing a benzophenone structural unit in the middle part of the chain and with the consideration on a possible initiation mechanism of the polymerization.

Experimental

Materials. Styrene (St) and methyl methacrylate (MMA) were purified by the usual methods. Tetrahydrofuran (THF) was distilled after refluxing with sodium. Each monomer and the solvent were directly introduced into a polymerization vessel by distillation from calcium hydride and from sodium-benzophenone, respectively, after evacuation by repeating freezing and thawing in a vacuum line (10^{-6} mmHg).

2,4′-Dichlorobenzophenone (DCBP) was recrystallized from petroleum ether. Methyl phenyl isopropenyl ether was synthesized according to the method of

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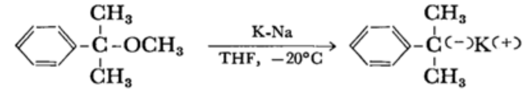
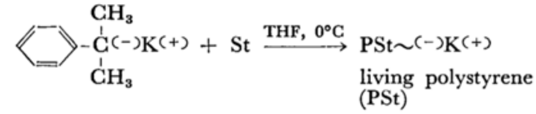
Ziegler and Dislich.[19]

Polymerization Procedures. General experimental techniques for a homogeneous anionic polymerization developed by Szwarc *et al.*[20] and by Morton *et al.*[21] were employed in the present investigation. Phenyl isopropyl potassium was prepared by the reaction of methyl phenyl isopropenyl ether with potassium-sodium alloy in THF *in vacuo*. This solution was filtered through a sintered glass filter to remove a small amount of potassium methoxide formed in the reaction.



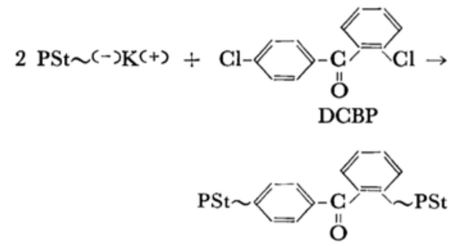
$$C_6H_5\text{-}C(CH_3)_2\text{-}OCH_3 \xrightarrow[\text{THF, }-20^\circ C]{\text{K-Na}} C_6H_5\text{-}C(CH_3)_2{}^{(-)}K^{(+)}$$

One-ended living polystyrene (PSt) prepared from the reaction of St with phenyl isopropyl potassium in THF was coupled with DCBP resulting in the formation of polystyrene ketone (PSt(CO)) having one carbonyl group in the middle part of the chain. In the coupling reaction two procedures were adopted, *i. e.* i) the solution of the coupling agent was added slowly to the solution of living polystyrene until its red color disappeared and ii) reversely, the solution of living PSt was added to the solution of the coupling agent.



$$C_6H_5\text{-}C(CH_3)_2{}^{(-)}K^{(+)} + St \xrightarrow{\text{THF, }0^\circ C} PSt\sim{}^{(-)}K^{(+)}$$

living polystyrene (PSt)



polystyrene ketone (PSt (CO))

Fractional precipitation of the coupling reaction product was made using benzene as a solvent and methanol as a precipitant at room temperature.

Potassium ketyl of PSt ketone was obtained by the treatment of PSt ketone with an equivalent amount of potassium naphthalene in THF. Potassium dianion of PSt ketone was also prepared by the reaction of PSt ketone with an excess of potassium in THF and the solution was filtered through a sintered glass filter to remove excess potassium.

The polymerization of MMA initiated by these adducts was performed in a vacuum system at room temperature. The resulting gross polymer was separated into four fractions using an extraction technique. Number average molecular weights of polymers were measured in benzene at 25°C using Hewlett-Packard 302 Vapour Pressure Osmometer (VPO).

Results and Discussion

Preparation of Polystyrene Ketone. Phenyl isopropyl potassium was prepared by the reaction of methyl phenyl isopropenyl ether with potassium-sodium alloy in THF. One-ended living PSt was prepared by the polymerization of St in THF with the use of phenyl isopropyl potassium. The results are shown in Tables 1 and 2.

PSt ketone having a benzophenone structural unit in the middle part of the chain was obtained by the stoichiometric coupling reaction of the living PSt with DCBP. The results of the coupling reactions are shown in Table 3.

The number average molecular weights Mn of the products are considerably smaller than the value, 1800, for PSt ketone calculated from Mn of starting living PSt. It is likely that unreacted PSt or mono-substituted PSt may also be contained in the product because of the low rate of coupling reaction of living PSt with DCBP.

Comparing A with B there is a difference in Mn of the products. It seems probable in the coupling reaction that the substitution reaction of living PSt with two chlorine atoms is in competition with the addition reaction of living PSt to a carbonyl group in DCBP. When an excess amount of living PSt is added to DCBP, tri-chain PSt would be formed.

Fractional precipitation for the coupling reaction

TABLE 1. PREPARATION OF PHENYL ISOPROPYL POTASSIUM

Methyl phenyl isopropenyl ether ml	THF ml	K : Na g	Temp. °C	Time hr
10.0	99.2	9.82 : 2.44	−20	40

TABLE 2. PREPARATION OF ONE-ENDED LIVING POLYSTYRENE

Phenyl isopropyl potassium-THF soln. ml	St g	THF ml	Temp. °C	Time hr	Concn. of living PSt mol/l	Mn of PSt[a]
74.3	21.09	305.0	0	3	7.71×10^{-2}	810

a) VPO; benzene; 25°C.

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Table 3. Coupling reaction of living polystyrene with 2,4′-dichlorobenzophenone

Run[a)]	Living PSt-THF soln. ml	PSt g	DCBP-THF soln. ml	DCBP g	Temp. °C	Time hr	Gross polymer Yield, g	Mn[b)]
A	278.4	17.80	110.0	2.73	25	5	20.40	1067
B	88.8	5.55	103.8	0.86	0	5	5.35	1460

a) A, The solution of living PSt in THF was added into the solution of DCBP in THF.
B, The solution of DCBP in THF was added into the solution of living PSt in THF.

b) VPO; benzene; 25°C.

Table 4. Fractionation of coupling reaction products

A) Original gross polymer, 20.25 g; benzene, 100 m*l*

Fr.	MeOH m*l*	Wt g	Mn
1	75	3.30	2310
2	90	3.56	2170
3	105	2.15	1970
4	130	1.86	1810
5	170	1.03	1740
6	MeOH insol.	4.86	960
Total		16.76[a)]	

a) Methanol soluble fraction was accidentally lost.

B) Original gross polymer, 5.20 g; benzene, 25 m*l*

Fr.	MeOH m*l*	Wt g	Mn
1	25	2.66	2230
2	50	1.00	2030
3	100	0.33	1670
4	MeOH insol.	0.36	1260
5	MeOH sol.	0.64	684
Total		4.99	

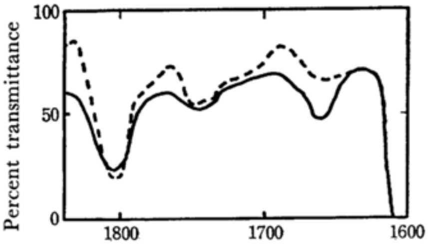


Fig. 1. Infrared spectra of polystyrene ketone and polystyrene.
——, Polystyrene ketone (A-5); ----, polystyrene

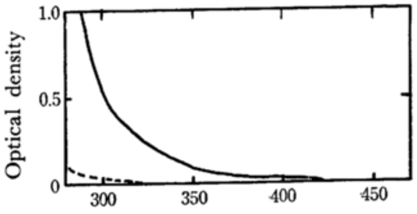


Fig. 2. UV- and visible absorption spectra of polystyrene ketone and polystyrene (in THF).
——, Polystyrene ketone (A-4) (10.0 mg/10 m*l* THF); ----, polystyrene (10.7 mg/10 m*l* THF)

product was carried out using benzene as a solvent and methanol as a precipitant at room temperature. These results are shown in Table 4.

The molecular weight of PSt ketone is calculated to be 1800 from the number average molecular weight of starting living PSt. Therefore, the values of molecular weights of Fr. 1 and Fr. 2 in both A- and B series may suggest that they contain tri-chain PSt. On the other hand, low molecular weight fractions Fr. 6 of A, Fr. 4 and 5 of B are considered to consist mainly of "mono"PSt.

Infrared-, UV- and visible absorption spectra of PSt ketone are shown in Figs. 1 and 2.

The stretching vibration of the carbonyl group in PSt ketone appears at 1660 cm^{-1} in the IR spectrum. It is known that the absorption based on the n–π^* transition of the carbonyl group of benzophenone exists at 330 mμ. PSt gives no absorption in UV- and visible absorption spectra. Therefore

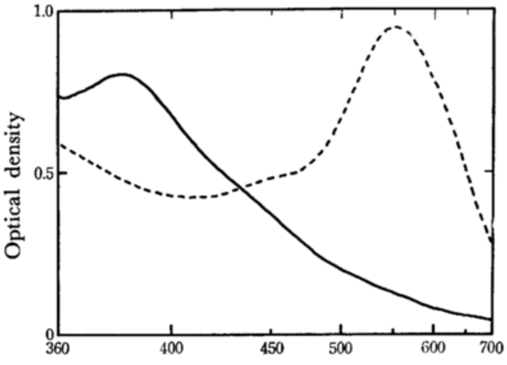


Fig. 3. Visible absorption spectra of polystyrene ketone potassium ketyl and polystyrene ketone potassium dianion (Solvent, THF).
——, PSt(CO)-K ketyl; ----, PSt(CO)-2K dianion

TABLE 5. PREPARATIONS OF POLYSTYRENE KETONE POTASSIUM ADDUCTS

PSt(CO) g	PSt(CO)-THF soln., m*l*	Potassium or potassium complex	Temp. °C	Time hr	Color	PSt(CO)-K adduct
0.920(A-5)	84.4	K-Naphthalene	r.t.[a]	5	dark yellow	PSt(CO)-K ketyl
1.645(A-4)	120.4	K	0	2	purple	PSt(CO)-2K dianion

a) Room temperature.

TABLE 6. POLYMERIZATIONS OF METHYL METHACRYLATE WITH POLYSTYRENE KETONE POTASSIUM ADDUCTS

PSt(CO)-K adduct-THF soln.[a] m*l*	PSt(CO) g	MMA g	THF m*l*	Temp. °C	Time hr	Yield g	Convn. of MMA %
84.4 (I)	0.92	1.53	41.6	22	1	2.34	92.8
100.9 (II)	1.38	2.06	53.1	23	1	3.15	86.0

a) I, polystyrene ketone potassium ketyl; II, polystyrene ketone potassium dianion.

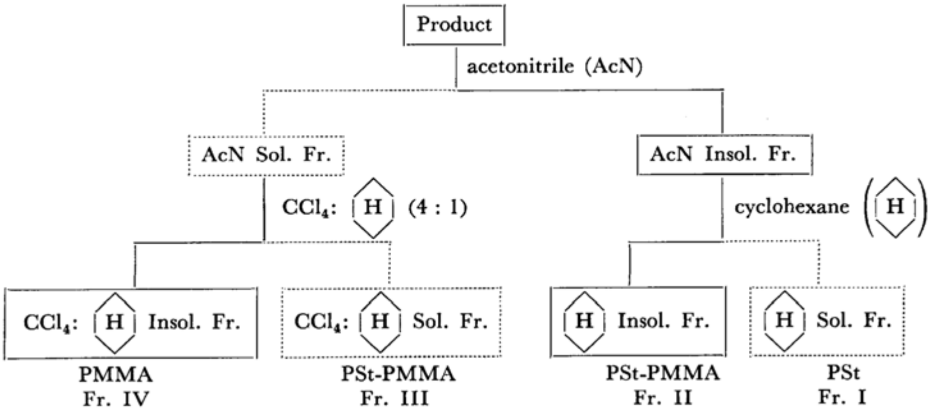


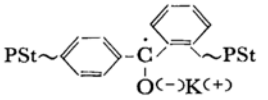
Fig. 4. An elution-fractionation scheme for the product in the system of methyl methacrylate-polystyrene ketone potassium adduct.
——, Insoluble fraction; ………, soluble fraction

a broad absorption band in the region of 330 to 450 mμ may be considered to be characteristic of PSt ketone. It is clear from these facts that a benzophenone structural unit enters in the PSt chain.

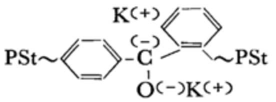
Preparations of Polystyrene Ketone Potassium Adducts. Table 5 represents the conditions of the reactions of PSt ketone with an equivalent amount of potassium-naphthalene or excess potassium in THF.

Figure 3 illustrates visible absorption spectra of PSt ketone potassium adducts.

The maximum absorptions appear at 384 mμ for dark yellow solution of the potassium ketyl and at 545 mμ for purple solution of the potassium dianion of PSt ketone. The change of the color from dark yellow to purple is observed by the addition of the THF solution of potassium naphthalene into the THF solution of PSt ketone potassium ketyl. These maximum absorptions are respectively in accord with those of benzophenone potassium ketyl at 382 mμ and benzophenone potassium dianion at 536 mμ.



polystyrene ketone potassium ketyl

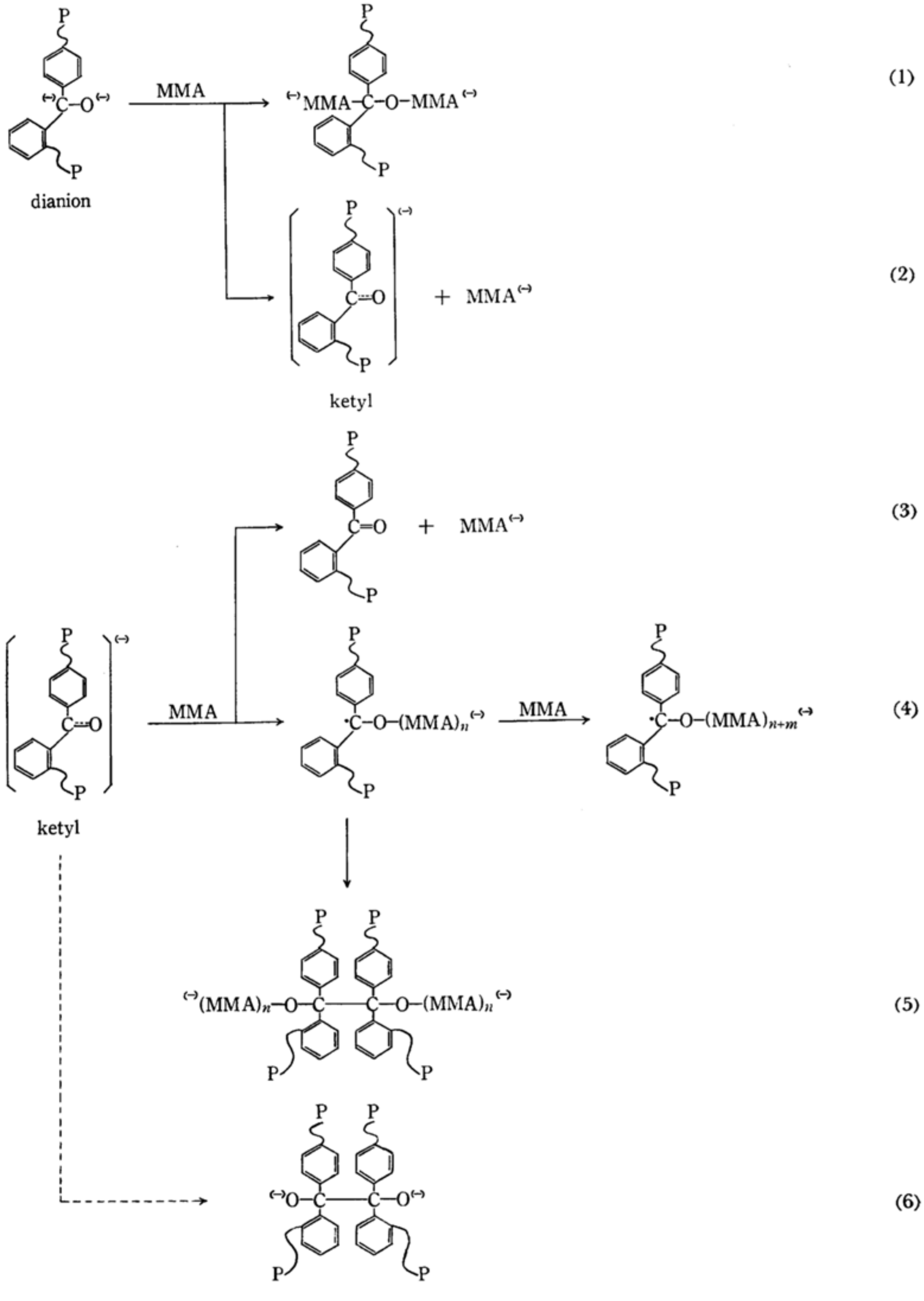


polystyrene ketone potassium dianion

Polymerization of Methyl Methacrylate with Polystyrene Ketone Potassium Adducts. The results of the polymerization of MMA with PSt ketone potassium adducts are shown in Table 6.

A gross polymer obtained in the PSt-MMA system was elution-fractionated using acetonitrile, cyclohexane and carbon tetrachloride - cyclohexane (4 : 1) as solvents into four fractions as shown in Fig. 4.

In Table 7 are presented the compositions and the molecular weights of the fractions determined by infrared analysis, elementary analysis and vapor pressure osmometry. The composition of Fr. I, as seen in the table, consists almost all of PSt. The molecular weight of Fr. I was higher than that of the parent PSt ketone. Therefore the formation of tetrachain PSt of benzpinacol type structure, to which extremely short MMA chain may attach, and its inclusion in this fraction may be considered (*cf.* reaction (5)). Fr. IV was confirmed to be polymethyl methacrylate (PMMA) from the results of infrared- and elementary analyses. The PSt-PMMA graft copolymer must be contained in



P, polystyrene chain

TABLE 7. COMPOSITIONS AND MOLECULAR WEIGHTS OF THE FRACTIONS

Initiator		Fr. I	Fr. II	Fr. III	Fr. IV
PSt(CO)-2K dianion	Wt, g (%)	0.60(20.8)	0.21(7.3)	1.50(51.9)	0.58(20.0)
	Mn (VPO)	2590	6010	3630	8710
	St content[a] (wt%)	87.9	39.1	19.2	0
PSt(CO)-K ketyl	Wt, g (%)	0.27(11.5)	0.02(0.9)	1.61(68.8)	0.44(18.8)
	Mn (VPO)	2500	—	2400	10000
	St content[b] (wt%)	>90	40.4	41.9	0

a) Calcd. from elementary analysis data.

b) Calcd. using calibration curve of optical density ratio (D_{700}/D_{1720}).

Fr. II and III. The fact that the molecular weight of Fr. III is much smaller than that calculated from its St content might be attributed to the intermixing of low molecular weight PMMA.

From the experimental results described above possible mechanisms of the polymerization are presumed as follows.

In the polymerizations of MMA initiated with PSt(CO)-K dianion and - ketyl, PSt and PMMA together with PSt-PMMA star-type graft copolymer were formed. PSt(CO)-K dianion would react with MMA to result in the formation of PMMA dianion through the bond-formation mechanism (1) and PSt(CO)-K ketyl and the monomer anion through the electron-transfer mechanism (2). The formation of PSt and PMMA suggests the occurrence of the electron transfer from PSt(CO)-K ketyl as shown in reaction (3).

PSt-PMMA graft copolymer may be produced by the bonding of MMA with alcoholate anion of PSt(CO)-K ketyl as represented in reaction (4).

Contrary to the case of an equilibrium between benzophenone-alkali metal ketyl and benzpinacolate, the presence of PSt substituted benzpinacolate was denied by means of the measurement of the molecular weight of killed PSt(CO)-K ketyl. The formation of PSt substituted benzpinacolate shown in reaction (6) is improbable. The molecular weight of Fr. I in Table 7 was higher than that of the parent PSt(CO). It is probable that PSt-PMMA graft copolymer formed in the reaction (5) may be partly included in Fr. I together with PSt(CO) formed in the reaction (3).

In view of so small a content, if any, of the graft copolymer with short MMA-grafts in Fr. I, it seems that the radical anion carrying extremely low molecular weight PMMA may be preferentially contributed to the further addition of MMA (reaction (4)) compared with reaction (5). The coupling reaction (5), however, may also be possible because of the decrease in the coulombic repulsion between the chain end anions. In conclusion both the electron transfer and the bond formation were ascertained to coexist in the intitations of MMA with use of PSt(CO)-K ketyl and dianion.