

Graft Copolymerization of Styrene with Carbon Black-Alkali Metal Complex

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Synopsis

It was found that an ion radical complex is formed by the reaction of carbon black with an alkali metal (Li, Na, K) in tetrahydrofuran. The graft copolymerization of styrene with carbon black was carried out using the ion radical complexes as initiator, and free polystyrene and carbon black-polystyrene graft copolymer were obtained. The identification of the graft copolymer with carbon black was carried out by fractionation and thermal degradation. The initiation activity of the alkali metals increased in the order $Li < Na < K$. The effect of the particle size of the carbon black on the graft copolymerization was studied.

INTRODUCTION

Recently, polymerization using various inorganic compounds and the graft polymerization of vinyl monomers on these particle surfaces have been reported. Solomon¹ studied the polymerization of styrene by sodium montmorillonite and proposed a radical-ion theory in which the polymerization is initiated by an electron transfer from sodium to aluminium. Bittles et al.² reported the polymerization of styrene by acid clay proposing an ion-polymerization theory.

The presence of hydrogen and aldehyde, hydroxyl, carboxyl, and carbonyl groups on the surface of carbon black particle was reported by Smith et al.³ Okita et al.,^{4,5} also reported the radical reaction of styrene on the surface of carbon black particles using a radical initiator. They obtained a graft polymer by adding carbon black in the reaction process of the thermal polymerization of styrene.

We have studied the graft polymerization of vinyl monomers using a complex obtained by the reaction of carbon black with an alkali metal in tetrahydrofuran (THF). The number of radicals in the complex obtained was found by ESR to increase with the reaction time of carbon black with sodium.

This paper deals with the formation of a complex in the presence of lithium, sodium or potassium and the graft copolymerization of vinyl monomers using the complex thus obtained.

EXPERIMENTAL

Materials

The carbon black used was commercial coconut carbon black supplied by the Takeda Pharmaceutical Co., and it was used after heating at 300°C for 10 hr.

Styrene (St) was washed with 10% aqueous caustic soda and then with water. It was dried over calcium chloride and then distilled in a nitrogen atmosphere at reduced pressure. Acrylonitrile, methyl methacrylate and isopren were used, after drying and purifying by usual methods.

Tetrahydrofuran (THF) was refluxed with sodium wire and distilled to obtain completely anhydrous THF. Benzene and other solvents were purified by the usual methods.

Methods

The carbon black-alkali metal complexes prepared by the reaction of carbon black (1.00 g) with alkali metals in 20 ml of THF at room temperature under a nitrogen atmosphere for a given time. The graft copolymerization of the monomer was carried out by adding the monomer to the reaction mixture, and the polymer obtained was precipitated by pouring into methanol, and filtered, washed, and dried.

The extraction of homopolymer from the polymer obtained was carried out with benzene in a Soxhlet extractor and was continued until no more polymer could be detected in the refluxing solvent.

The graft efficiency and the percentage grafting were calculated by using the following equations.

$$\text{graft efficiency (\%)} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of total polymer obtained}}$$

$$\text{percentage grafting (\%)} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of carbon black used}}$$

ESR spectra were run on a HITACHI NPV-3B spectrometer at 100 kc. The sample for ESR measurement was prepared from 1.0 g of carbon black and 0.1 g of sodium in THF.

Gas-chromatographic analysis was carried out with a DOP column (3 mm \times 2.25 m) after thermal degradation at 500°C, under a nitrogen atmosphere.

The intrinsic viscosity of polystyrene was measured in benzene solution, and the degree of polymerization was calculated from the following equation,⁶

$$\bar{P}_n = 1770 \times [\eta]^{1.40}$$

RESULTS AND DISCUSSION

ESR Measurement of Complexes

It was found by ESR measurement that radicals existed in the heated carbon black. The heated carbon black showed a Gaussian shape of 69

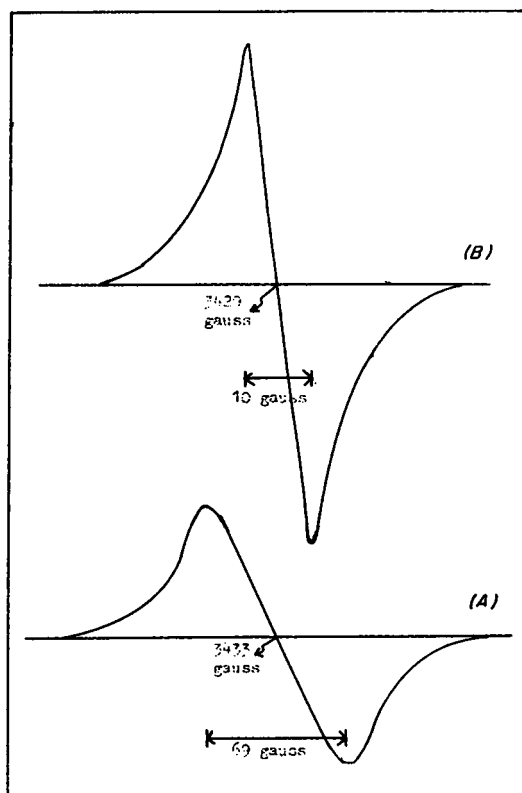


Fig. 1. ESR spectrum of nontreated carbon black (A) and sodium-treated carbon black (B).

gauss at 3433 gauss. But when carbon black was reacted with sodium in THF for 48 hr, the reaction product displayed a Lorentzian-shaped absorption peak with a line width of 10 gauss at 3429 gauss, as shown in Figure 1. The above results suggest the formation of new radicals on the carbon surface.

Table I shows the relative amount of radicals calculated from the area under the absorption curve. The amount of radicals for sodium-treated carbon was 1.9 relative to nontreated carbon, after 3 hr, and increased to

TABLE I
The Relative Amount of Radicals and Reaction Time

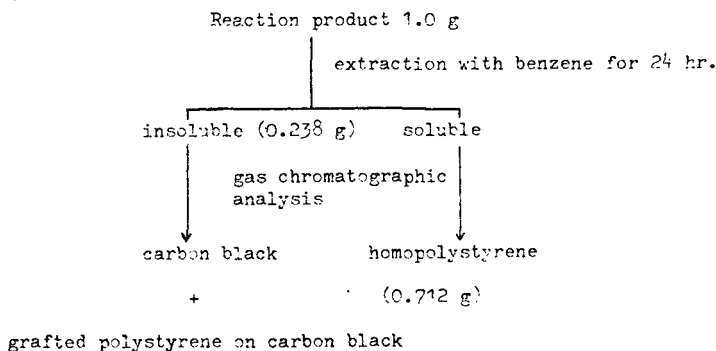
Sample	Reaction time of carbon black with Na	Relative amount of radicals
Nontreated carbon black	—	1
Na-treated carbon black	3	1.9
Na-treated carbon black	4.8	2.6

2.6 after 48 hr, i.e., the amount of radicals increased with the reaction time. From the result, it was suggested that an anion-radical complex could be formed on the carbon surface by an electron transfer from sodium to the carbon black.

Confirmation of Carbon Black Graft Copolymer

A complex was prepared by the reaction of carbon black (1.0 g) with sodium (0.1 g) in 20 ml of HTF, at room temperature under a nitrogen atmosphere for 24 hr. Then styrene (5 ml) was added to the complex and was allowed to polymerize for 5 hr at room temperature. Of the above polymerized product 1.00 g was extracted with benzene. An insoluble portion (carbon black) and carbon graft copolymer of 0.2389 g was obtained from 0.182 g of starting carbon black (Fig. 2A). On the other hand, in the case where 0.182 g of carbon black was mixed with 0.818 g of polystyrene in THF for 5 hr, 0.166 g of insoluble matter (carbon black) was recovered from 1.00 g of the mixture (Fig. 2B). Whether the insoluble

(A)



(B)

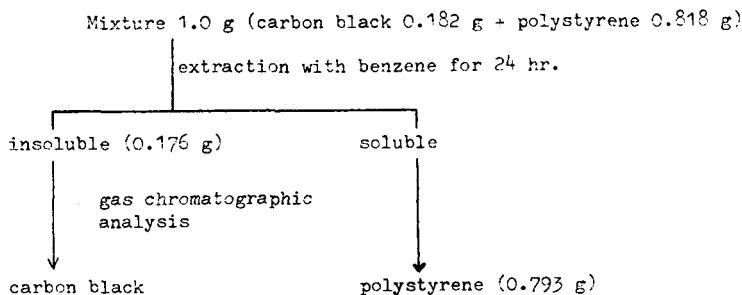


Fig. 2. Extraction method.

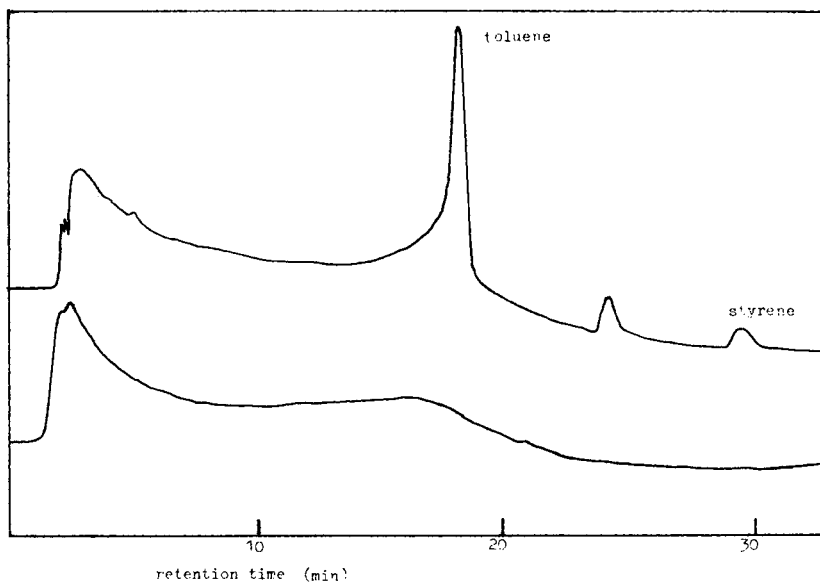


Fig. 3. Gas-chromatographic analysis of insoluble fraction of reaction product: 2.41 mg. (A) and of mixture: 2.69 mg. (B) in Fig. 2.

portion was graft copolymer or not was determined by gas chromatography. The former insoluble portion showed peaks attributable to toluene and styrene, the thermal degradation products of polystyrene (Fig. 3A) but the latter insoluble portion did not (Fig. 3B), indicating that there was absorption of styrene on the carbon black surface.

The reaction product, which contained unreacted carbon black, of the carbon black-sodium complex with styrene was considered to be carbon graft copolymer with polystyrene by chemical bond on the surface of carbon black.

Graft Copolymerization of Styrene

A carbon black-alkali metal complex was allowed to polymerize with styrene in 20 ml of THF at room temperature under a nitrogen atmosphere for 3–12 hr. The reaction product was precipitated in methanol, dried in vacuo and extracted with benzene. In Table II and Figure 4, the graft efficiency and the percentage grafting with time are shown.

The graft efficiency and the percentage grafting increased with time. The graft percentage was 38.65% at the completion of polymerization and the intrinsic viscosity of the polystyrene obtained by homopolymerization with the sodium that did not react with carbon black was 0.68.

In order to investigate whether the graft copolymer was obtained from a living polymer that had reacted with functional groups on the surface of the carbon black particles, the following experiment was performed. Naphthalene, 0.34 g (2.6×10^{-3} mole), and sodium, 0.05 g (2.2×10^{-3} mole),

TABLE II
The Polymerization of Styrene with Na-treated Carbon Black^a

Polymerization time, hr	St conversion, %	Graft efficiency, %	Percentage grafting, %	$[\eta]$ dl/g of free PST	\bar{P} of free PST
3	95.01	5.01	29.65	0.670	1010
6	100.00	8.51	38.65	0.685	1040
9	100.00	8.68	38.90	0.683	1040
12	100.00	8.64	38.83	0.689	1050

^a Carbon black: 1.0 g (8.3×10^{-2} mole), sodium: 0.1 g (4.3×10^{-3} mole), styrene: 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature.

were allowed to react in 20 ml of THF at room temperature under a nitrogen atmosphere for 6 hr, and 2.5 ml (2.2×10^{-3} mole), of styrene was added. To this reddish living polystyrene solution was added 0.05 g of carbon black, with stirring (Table III).

It was found that the graft copolymer was obtained by reaction with the functional groups on the surface of the carbon black particles.

In the case where a carbon black-sodium complex and styrene were reacted, the graft percentage was 35% (Fig. 4). When the living polystyrene was used instead of styrene, its graft percentage was 18.79% (Table III).

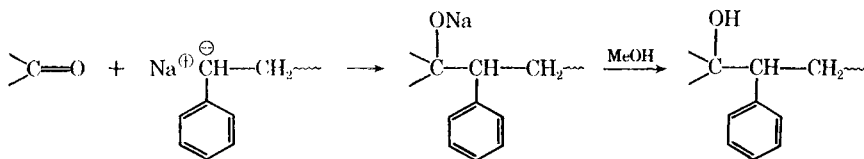
TABLE III
Reaction of Living Polystyrene and Carbon Black^a

Reaction time of living polystyrene with carbon black	St conversion, %	Graft efficiency, %	Percentage grafting	$[\eta]$ de/g of PST	\bar{P} of PST
0.5	100	2.26	10.15	0.709	1090
2.5	100	3.62	16.31	0.710	1100
4.5	100	4.18	18.79	0.710	1100

^a Sodium: 0.05 g (2.2×10^{-3} mole), naphthalin 0.34 g (2.6×10^{-3} mole), styrene: 2.5 ml (2.2×10^{-2} mole), 20 ml of THF, carbon black: 0.5 g., at room temperature.

This result indicates that about 50% of the graft copolymer obtained from the carbon black-sodium complex, i.e., the grafted polystyrene was propagated from ion radicals on the surface of carbon particle, and the rest of the graft copolymer originated from living polystyrene.

It may be supposed that living polystyrene may add to a carbonyl or quinone group, one of the functional groups on the surface of a carbon black particle as follows:



Effect of the Amount of Styrene on Graft Copolymerization

One to 10 ml of styrene was added to a constant amount of the carbon black-sodium complex and was allowed to react for 6 hr. The graft efficiency and the percentage grafting are shown in Table IV and Figure 5.

TABLE IV
Relationship Between Graft Copolymerization and Amount of Styrene^a

Amount of styrene, ml	St conversion, %	Graft efficiency, %	Percentage grafting, %	$[\eta]$ dl/g of free PSt	\bar{P} of free PSt
1	93.87	6.57	5.59	0.229	230
2	100.0	6.46	11.69	0.410	510
4	100.0	5.13	18.57	0.600	890
6	100.0	6.34	34.52	0.728	1140
8	100.0	6.24	45.14	0.936	1610
10	100.0	5.38	48.99	1.165	2190

^a Carbon black: 1.0 g (8.3×10^{-2} mole), sodium: 0.1 g (4.3×10^{-3} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

As the amount of styrene increased, the graft percentage increased with the increase in the degree of polymerization of styrene propagated on the surface of the carbon particles. The intrinsic viscosity of homopolystyrene and the degree of polymerization of styrene correlated directly with the amount of styrene.

The carbon black-alkali metal complex was allowed to react with different kinds of monomer in 20 ml of THF, at room temperature under a nitrogen atmosphere for 6 hr. The results are shown in Table V.

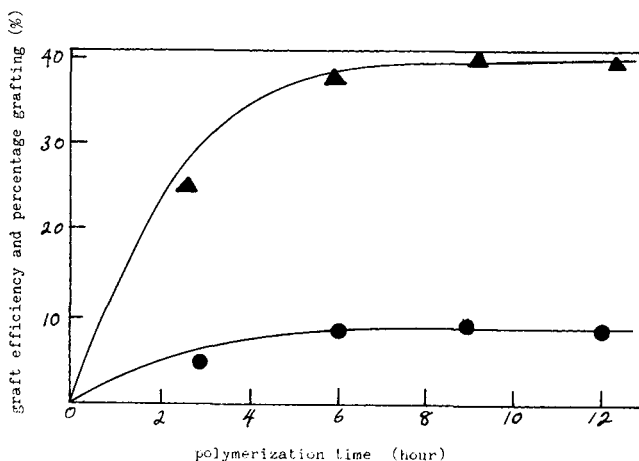


Fig. 4. Relationships between: (●), graft efficiency, and (▲), percentage grafting and polymerization time of styrene. Carbon black 1.0 g (8.3×10^{-2} mole), sodium 0.1 g (4.3×10^{-3} mole), styrene 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature.

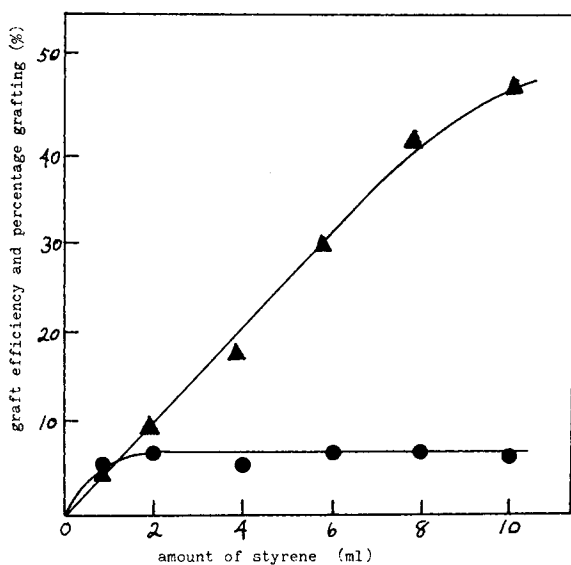


Fig. 5. Relationships between: (●), graft efficiency, and (▲), percentage grafting and amount of styrene. Carbon black 1.0 g (8.3×10^{-2} mole), sodium 0.1 g (4.3×10^{-2} mole), in 20 ml. of THF, at room temperature. Polymerization time: 6 hr.

TABLE V
Graft Copolymerizations of Various Monomers at Room Temperature^a

Monomer	Monomer conversion, %	Graft efficiency, %	Percentage grafting, %
Acrylonitrile ^b	54.1	33.80	48.17
Methyl methacrylate	32.9	6.61	8.15
Styrene	100.0	8.68	39.25
Isoprene	70.8	3.09	6.95

^a Amount of additional monomer: 4.3×10^{-2} mole, carbon black: 1 g, Na 0.1 g, in 20 ml of THF, polymerization time: 6 hr.

^b Extraction solvent used: dimethylformamide.

Effect of the Amount of Sodium on Graft Copolymerization

Various amounts of sodium were used with a constant amount of carbon black for producing carbon black-sodium complexes. The complexes were then reacted with 5 ml of styrene for 6 hr (Table VI).

No polymerization occurred in the absence of sodium. With less than 60 mg of sodium, the graft efficiency and the percentage grafting were found to be very low and the degree of polymerization was around 100. This may result from the poor formation of ion radicals by the elimination of sodium in the reaction mixture by some unknown factors. The graft efficiency and the percentage grafting increased with the amount of sodium.

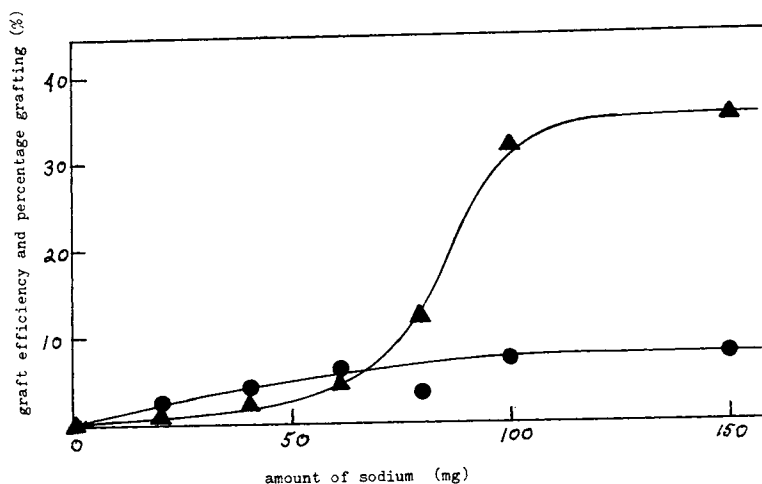


Fig. 6. Relationships between: (●), graft efficiency, and (▲) percentage grafting and amount of sodium. Carbon black 1.0 g (8.3×10^{-2} mole), styrene 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

TABLE VI
Relationship Between Graft Copolymerization and Amount of Sodium^a

Amount of Na, mg	St conversion, %	Graft efficiency, %	Percentage grafting, %	$[\eta]$ dl/g of free PSt	\bar{P} of free PSt
0	0	—	—	—	—
20	6.07	1.90	0.52	—	—
40	7.51	3.82	2.19	0.110	80
60	7.88	7.01	1.45	0.157	130
80	100.00	2.81	12.71	0.660	990
100	100.00	7.37	33.37	0.659	990
100	100.00	7.75	35.08	0.662	990

^a Carbon black: 1.0 g (8.3×10^{-2} mole), styrene: 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

The degree of polymerization increased up to 990. At the completion of polymerization, the intrinsic viscosity was about 0.66.

Effect of Various Alkali Metals on Graft Copolymerization

Carbon black-alkali metal complexes were formed using lithium, sodium, and potassium. Polymerization of styrene was carried out using these complexes as shown in Table VII and Figure 7.

As shown in Figure 7, when the alkali metal was allowed to react with carbon black in THF for 24 hr, the graft percentages were found to be 17.62% for lithium, 26.42% for sodium, 43.65% for potassium. The initiation activity of the alkali metals increased in the order $\text{Li} < \text{Na} < \text{K}$. It is considered that this difference in the graft efficiency results from ion-

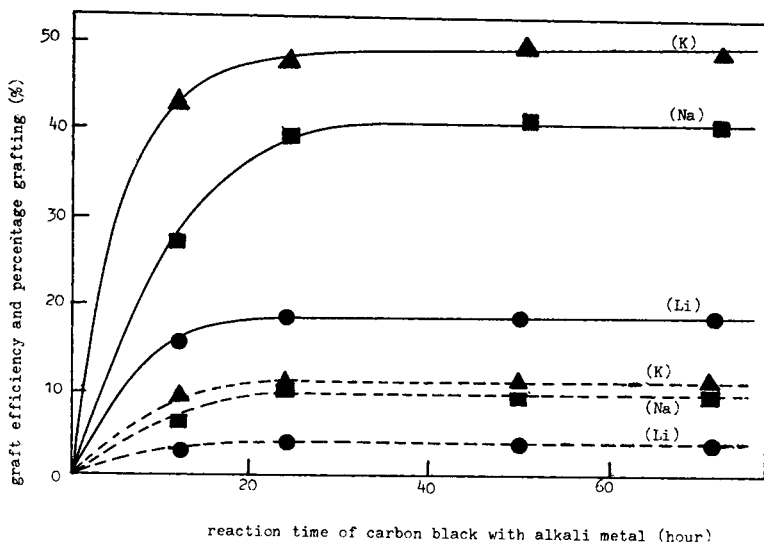


Fig. 7. Relationships between: (---), graft efficiency, and (—), percentage grafting and various alkali metal. Carbon black 1.0 g (8.3×10^{-2} mole), alkali metal (4.3×10^{-3} mole), styrene 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

ization series rather than solvation. The intrinsic viscosity did not correlate with the sort of alkali metal or with the reaction time of the metals with carbon black.

TABLE VII
Effect of Various Alkali Metals on Graft Copolymerization with Carbon Black^a

	Reaction time, hr	St conversion, %	Graft efficiency, %	Percentage grafting, %	$[\eta]$ dl/g of free PSt	\bar{P} of free PSt
C-Li	12	100	3.89	17.62	0.619	900
	24	100	3.92	17.73	0.611	890
	48	100	4.02	18.18	0.623	910
	72	100	3.99	18.07	0.640	950
C-Na	12	100	5.84	26.42	0.651	970
	24	100	8.68	39.25	0.682	1040
	48	100	8.81	39.85	0.650	970
	72	100	8.84	40.02	0.672	1000
C-K	12	100	9.65	43.65	0.630	930
	24	100	10.55	47.73	0.635	940
	48	100	10.73	48.56	0.636	940
	72	100	10.77	48.73	0.632	930

^a Carbon black: 1.0 g (8.6×10^{-2} mole), Li, Na, and K: 4.3×10^{-3} mole, styrene: 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

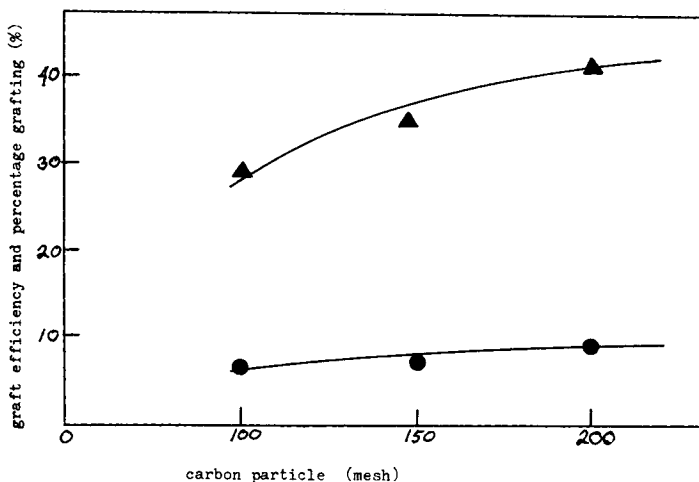


Fig. 8. Relationships between: (●), graft efficiency, and (▲), percentage grafting and particle size of carbon black. Carbon black 1.0 g (8.3×10^{-2} mole), sodium 0.1 g (4.3×10^{-3} mole), styrene 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

Effect of Particle Size of Carbon Black on Graft Copolymerization

The effect of the particle size of the carbon black on initiation activity was studied using carbon black of particle size 100, 150, and 200 mesh. Carbon black and sodium were allowed to react in THF for 24 hr and the polymerization was carried out by adding styrene to this reaction mixture at room temperature and reacting for 6 hr (Table VIII, Fig. 8). It was found that the graft efficiency and the percentage grafting increased with decrease in the particle size. This is probably due to an increase in the number of active sites with a decrease in particle size.

The result indicates that graft copolymerization did not occur at the carbon lamella, and therefore it could be initiated either from active sites on the particle surface or from addition of living polymer to the functional groups on the surface of carbon particles.

TABLE VIII
Relationship Between Graft Polymerization and Particle Size of Carbon Black*

Particle size (mesh)	St conversion, %	Graft efficiency, %	Percentage grafting, %	$[\eta]$ dl/g of free PSt	\bar{P} of free PSt
100	100.0	6.52	29.50	0.665	1000
100	100.0	7.81	35.36	0.658	990
200	100.0	9.10	41.16	0.659	990

* Carbon black: 1.0 g (8.3×10^{-2} mole), sodium: 0.1 g (4.3×10^{-3} mole), styrene: 5 ml (4.3×10^{-2} mole), in THF, at room temperature. Polymerization time: 6 hr.

Graft Copolymerization of Styrene with Various Kinds of Carbon Black

It was investigated whether the graft efficiency and the percentage grafting differ with different kinds of carbon black.

In graphite, the network planes consist of condensed rings of benzene which constitute a regular three dimensional structure. While the amorphous carbons, acetylene black, active carbon, and coconut carbon, have an irregular three dimensional structure.

All the kinds of carbon black were extracted with acetone before use. The polymerization was carried out by adding styrene to the carbon black-alkali metal complex (Table IX). The graft efficiency and the percentage grafting in graphite were 7.54% and 33.94%, respectively. Whereas, the

TABLE IX
Graft Copolymerization of Styrene with Different Kinds of Carbon Black^a

Carbon black	St conversion %	Graft efficiency, %	Percentage grafting, %
Acetylene black	98.73	6.33	27.77
Graphite	99.42	7.54	33.94
Active black	100.00	7.01	31.71
Coconut black	100.00	9.65	43.65

^a Carbon black: 1.00 g (8.3×10^{-2} mole), sodium: 0.1 g (4.3×10^{-3} mole), styrene: 5 ml (4.3×10^{-2} mole), in 20 ml of THF, at room temperature. Polymerization time: 6 hr.

graft percentage of coconut black, active carbon and acetylene black was found to be 43.65%, 27.77%, and the graft efficiency 9.65–6.33%. No significant difference was observed between these four carbon blacks.

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