

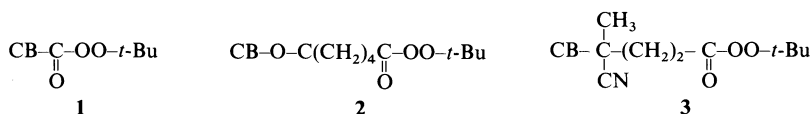
Radical Grafting from Carbon Black. Graft Polymerization of Vinyl Monomers Initiated by Peroxyester Groups Introduced onto Carbon Black Surface

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ABSTRACT: Carbon blacks having *tert*-butyl peroxyester groups (1, 2, and 3) were prepared by the reaction of acyl chloride



groups on carbon black with *tert*-butyl hydroperoxide. The introduction of acyl chloride groups onto carbon black was achieved by three methods: (1) reaction of a carboxyl group with thionyl chloride, (2) reaction of a phenolic hydroxyl group with adipoyl chloride, and (3) reaction of thionyl chloride with a carboxyl group introduced by the treatment of aromatic ring of carbon black with 4,4'-azobis(4-cyanovaleric acid). Carbon black **1** has no ability to initiate the graft polymerization of methyl methacrylate (MMA) because phenyl radical formed on the carbon black by decomposition of the peroxyester groups inhibited the polymerization. On the contrary, carbon blacks **2** and **3** were able to initiate the graft polymerization of MMA at 70–90°C and PMMA was effectively grafted onto the surface based on the propagation of the polymer from the alkyl radicals formed on the surface. The percentage of grafting of PMMA at 70°C by use of **3** as initiator increased to about 80% with progress of polymerization. Furthermore, the graft polymerization of several vinyl monomers initiated by **3** was investigated.

KEY WORDS Carbon Black / Graft Polymerization / Polymer-Grafted Carbon Black / Peroxyester Groups / 4,4'-Azobis(4-cyanovaleric acid) / Methyl Methacrylate / *tert*-Butyl Hydroperoxide /

The dispersibility of carbon black in a polymer matrix or an organic solvent is remarkably improved by the grafting of polymers onto the surface and increases with an increase in the percentage of grafting. To prepare polymer-grafted carbon black with a higher percentage of grafting, it is necessary to initiate the polymerization from active sites on the surface of carbon black. In a series of our papers, we reported anionic grafting from alkali metal carboxylate groups (COOM) on carbon black^{1,2} and cationic grafting from acylium perchlorate groups (CO⁺ClO₄⁻) on

carbon black.^{3,4} However, the radical grafting from carbon black has been scarcely investigated.

It is known that carbon black itself has an unpaired electron;⁵ however, the unpaired electron has no ability to initiate the radical polymerization of vinyl monomers, because the unpaired electron was stabilized by the polycondensed aromatic rings of carbon black. Therefore, the introduction of active radicals onto a carbon black surface is required for the radical grafting from carbon black.

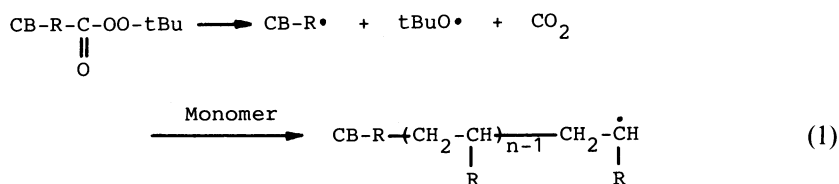
In the previous paper, we succeeded in the

radical graft polymerization of water-soluble monomers, such as acrylamide and acrylic acid, from carbon black by use of carbon black having hydroxyl alkyl groups/ceric ion redox initiating system.⁶ However, the redox system failed to initiate the graft polymerization of methyl methacrylate or styrene.

It has been reported the polymerization of vinyl monomers is initiated by polymer having peroxyester groups, introduced by the reaction of acyl chloride groups of the polymer with

tert-butyl hydroperoxide, to give graft copolymer.⁷⁻⁹ Furthermore, the grafting of vinyl polymers onto carbon fiber by use of peroxyester groups on the fiber was reported.¹⁰

In the present paper, the radical graft polymerization of various kinds of vinyl monomers, such as MMA and styrene, from carbon black initiated by peroxyester groups introduced onto the surface was investigated (eq 1).



EXPERIMENTAL

Materials

The carbon blacks used were furnace black Philblack O (Philips Petroleum Co., BET specific surface area, $79.6 \text{ m}^2 \text{ g}^{-1}$) and channel black Neospectra II (Columbian Carbon Co., $906 \text{ m}^2 \text{ g}^{-1}$). Philblack O was extracted with benzene to remove the resinous substances present on the surface. These carbon blacks were dried *in vacuo* at 110°C before use.

Methyl methacrylate (MMA), methyl acrylate, acrylonitrile, styrene, vinyl acetate, and *N*-vinyl-2-pyrrolidone were purified by general methods and distilled twice.

tert-Butyl hydroperoxide (*t*-BuOOH) obtained from Aldrich Chemical Co. was purified by distillation under reduced pressure. 4,4'-Azobis(4-cyanovaleric acid) (ACV) obtained from Aldrich Chemical Co. was recrystallized from methanol. Adipoyl chloride was prepared by the reaction of adipic acid with thionyl chloride by the ordinary method.

Introduction of Carboxyl Groups onto Carbon Black

The introduction of carboxyl groups onto carbon black was achieved by the reaction of carbon black with 4-carboxy-2-cyano-2-butyl radical which formed by the thermal decomposition of ACV.

Into a 500 ml flask, 6.0 g of carbon black, 0.40 g of ACV, and 100 ml of benzene were charged. The reaction mixture was stirred at 60°C under nitrogen. Then 0.40 g of ACV was added to the reaction mixture every 8 h and the reaction was allowed to continue for 56 h (total ACV used for the treatment was 2.8 g). The resulting carbon black was purified by Soxhlet extraction with acetone and dried *in vacuo*. The amount of carboxyl groups introduced onto carbon black was determined by nitrogen analysis.¹¹

Introduction of Acyl Chloride Groups onto Carbon Black

Carbon black having acyl chloride groups was prepared by the reaction of carboxyl groups with thionyl chloride. The procedure was described in detail in the previous paper.^{3,4}

In addition, the introduction of acyl chloride groups onto carbon black by the reaction of phenolic hydroxyl groups with adipoyl chloride was carried out as follows: Into a 100 ml flask, 2.0 g of carbon black, 1.0 ml of adipoyl chloride, 30.0 ml of dioxane, and 0.1 ml of pyridine were charged. The mixture was stirred at 50°C for 24 h under dry nitrogen. After the reaction, the resulting carbon black was filtered, washed with absolute dioxane and dried *in vacuo*.

Introduction of tert-Butyl Peroxyester Groups onto Carbon Black

The introduction of *tert*-butyl peroxyester groups onto carbon black was achieved by the reaction of acyl chloride groups on the surface with *t*-BuOOH. A typical example is as follows: Into a 100 ml flask, 2.0 g carbon black having acyl chloride groups, 1.0 ml of *t*-BuOOH, 20.0 ml of dioxane, and 0.1 g of sodium hydroxide were charged. The reaction was conducted at 20°C for 12 h under stirring with a magnetic stirrer. After the reaction, the resulting carbon black was poured into methanol, filtered, washed with methanol and acetone, and dried *in vacuo* at room temperature. The treated carbon black was stored in

the dark at below 0°C.

Determination of Content of tert-Butyl Peroxyester Groups on Carbon Black

Carbon black having *tert*-butyl peroxyester groups was stirred with excess of KI aqueous solution (0.01 mol l⁻¹) at room temperature for 3 h. Then excess of KI was titrated with aqueous AgNO₃ solution (0.01 mol l⁻¹) and aqueous KSCN solution (0.01 mol l⁻¹) according to the method of Volhard.¹² The content of *tert*-butyl peroxyester groups on carbon black was calculated from the amount of KI consumed by the carbon black.

Polymerization Procedures

Into a glass tube, 0.50 g of carbon black and 10.0 ml of MMA were charged. The tube was cooled in a dry ice/methanol bath, thawed three times with nitrogen, and sealed under vacuum. The sealed tube was heated at 70°C with shaking. After polymerization, the contents of the tube were poured into a large excess of methanol to precipitate the polymer and carbon black. The precipitate was filtered, washed with methanol, and dried *in vacuo*. The conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Precipitate obtained (g)} - \text{Carbon black (g)}}{\text{Monomer used (g)}} \times 100$$

Determination on Percentage of Grafting

To separate the ungrafted polymer from the reaction product that contained carbon black, the product was dispersed in chloroform and centrifuged at 1.2×10^4 rpm until carbon black was precipitated completely. The carbon black

precipitate was extracted with chloroform by a Soxhlet extractor until no more polymer could be detected in the refluxing solvent. The percentage of grafting was determined by the following equation:

$$\text{Percentage of grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Carbon black used (g)}} \times 100$$

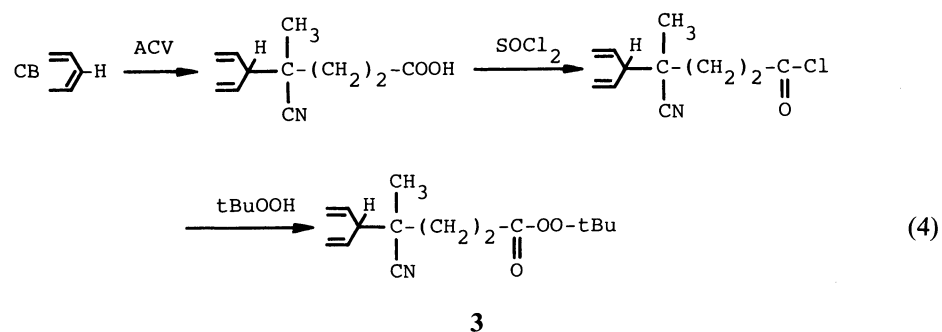
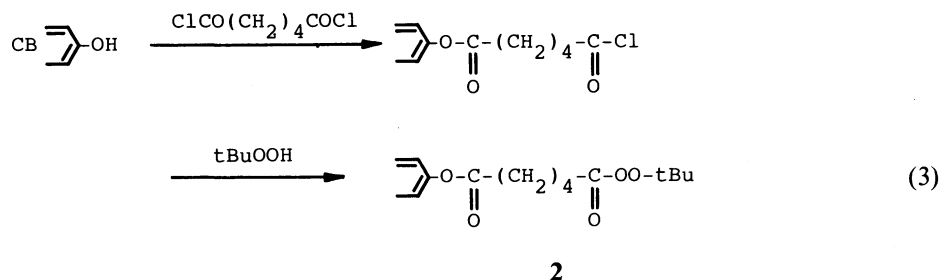
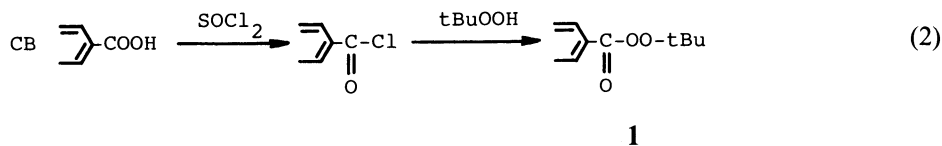
RESULTS AND DISCUSSION

Introduction of tert-Butyl Peroxyester Groups onto Carbon Black

It has been reported that peroxyester groups

can be introduced onto a polymer chain by the reaction of acyl chloride groups on the polymer with *t*-BuOOH.⁷⁻⁹ Therefore, the introduction of *tert*-butyl peroxyester groups onto carbon black by the reaction of acyl chloride groups on the surface with *t*-BuOOH

was examined.



The introduction of acyl chloride groups onto carbon black was achieved by the following three methods: (1) reaction of carboxyl groups on carbon black with thionyl chloride (eq 2), (2) reaction of phenolic hydroxyl groups on carbon black with adipoyl chloride (eq 3), and (3) reaction of 4-cyanovaleric acid groups, introduced by the reaction of ACV with carbon black, with thionyl chloride (eq 4). These carbon blacks having acyl chloride groups were treated with excess *t*-BuOOH in dioxane in the presence of sodium hydroxide at 20°C for 12 h.

The amount of *tert*-butyl peroxyester groups introduced onto carbon black surface determined by titration is shown in Table I. In Table I, it is apparent that peroxyester groups can be introduced onto channel black

Neospectra II by use of its carboxyl (eq 2) or phenolic hydroxyl groups (eq 3). However, peroxyester groups could not be introduced onto furnace black Philblack O by eq 2 or 3, because Philblack O has no carboxyl groups and fewer phenolic hydroxyl groups.

Therefore, the introduction of peroxyester groups onto Philblack O was achieved by use of Philblack O previously treated with ACV (eq 4).

Based on the above results, it is concluded that *tert*-butyl peroxyester groups can be introduced onto carbon black surface by the reaction of acyl chloride groups on the surface with *t*-BuOOH according to the methods shown in eq 2, 3, and 4.

Radical Grafting from Carbon Black

Table I. *tert*-Butyl peroxyester groups introduced onto carbon black surface

CB	COOH	OH	Introduction reaction	No.	Peroxyester group
	meq g ⁻¹	meq g ⁻¹ ^a			meq g ⁻¹
Neospectra II	0.40	0.24	—	—	0
Neospectra II	0.40	0.24	eq 2	1	0.20
Neospectra II	0.40	0.24	eq 3	2	0.18
Philblack O	0	0.02	eq 2	—	0
Philblack O	0	0.02	eq 3	—	0
Philblack O ^a	0.20	0.02	eq 4	3	0.15

^a Carboxyl groups were introduced by treatment with ACV.

Graft Polymerization of MMA Initiated by 1

The polymerization of MMA was carried out in the presence of **1** at 70°C and the initiating activity of **1** was examined. Table II shows the results of the polymerization of MMA initiated by **1**.

As shown in Table II, thermal polymerization of MMA proceeded even in the absence of initiator, whereas the rate of the polymerization was negligibly small. On the contrary, both in the presence of untreated carbon black and in the presence of **1**, the polymerization of MMA was completely inhibited.

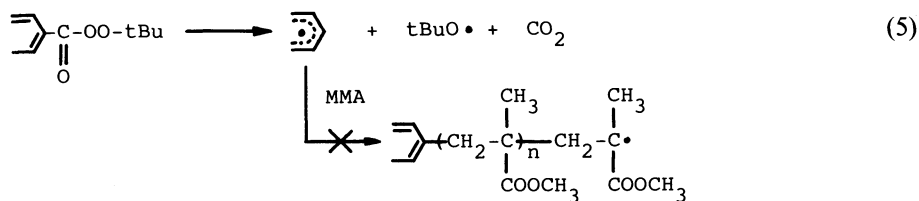
These phenomena suggest that in the presence of untreated carbon black, thermal polymerization is inhibited by oxygen con-

Table II. Graft polymerization of MMA initiated by **1**^a

CB	Conversion
	%
None	0.7
Neospectra II	0
<i>t</i> -BuOOCO-Neospectra II (1)	trace

^a Carbon black, 0.50 g; MMA, 10.0 ml; 70°C; 6 h.

taining groups on carbon black surface. On the other hand, in the presence of **1**, *tert*-butyl peroxyester groups are considered to decompose to give phenyl radical and *tert*-butyloxy radical (eq 5).⁸ The phenyl radical



seems to be stabilized by polycondensed aromatic rings of carbon black and has no ability to initiate the polymerization. Although the *tert*-butyloxy radical initiates the polymerization of MMA, the growing polymer radical may be immediately trapped by the phenyl radical.

Therefore, it is apparent that the graft po-

lymerization of vinyl monomers is unable to initiate by **1**.

Graft Polymerization of MMA Initiated by 2

The graft polymerization of MMA onto carbon black was examined by use of **2** as an initiator. Different from **1**, carbon black **2** was expected to generate *tert*-butyloxy radical and

Table III. Graft polymerization of MMA initiated by 2^a

CB	Conversion
	%
None	0.7
Neospectra II	0
<i>t</i> -BuOOH-adsorbed Neospectra II	0
<i>t</i> -BuOOCO-Neospectra II (2)	3.8

^a Polymerization conditions are given in Table II.

alkyl radical which has initiating activity of polymerization.

The results are shown in Table III. As mentioned above, in the presence of untreated carbon black, no polymerization could be detected at all. On the contrary, in the presence of 2, the polymerization of MMA was found to be initiated at 70°C.

To ensure initiation by *tert*-butyl peroxyester groups on 2, the initiating ability of *t*-BuOOH-adsorbed Neospectra II was evaluated. As shown in Table III, *t*-BuOOH-adsorbed carbon black failed to initiate the polymerization of MMA. This suggests that *t*-BuOOH adsorbed on carbon black surface during the treatment for the introduction of peroxyester groups is removed completely by washing with methanol and drying *in vacuo*.

Based on these results, it is concluded that carbon black having *tert*-butyl peroxyester groups, 2, has an ability to initiate the polymerization of MMA.

Figure 1 shows the time-conversion curves of the polymerization of MMA initiated by 2 at 70 and 90°C. As is seen in Figure 1, the polymerization was of the dead-end type and conversion did not increase even if the polymerization time was extended up to 6 h.

Smets *et al.* have reported that in the presence of carboxyl groups, peroxyester groups in polymer chain decompose very rapidly.⁷ Therefore, it is considered that in the polymerization initiated by 2, *tert*-butyl peroxyester groups on carbon black rapidly decom-

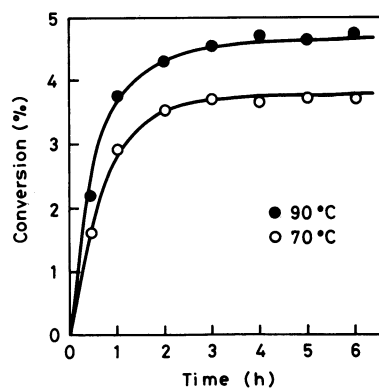


Figure 1. Graft polymerization of MMA initiated by 2. Carbon black, 0.50 g; MMA, 10.0 ml.

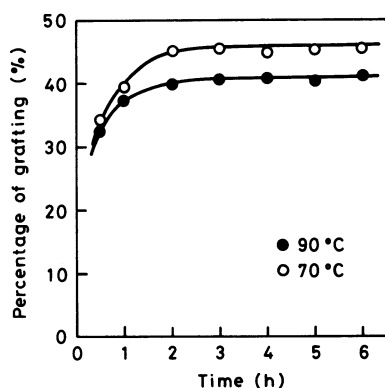


Figure 2. Relationship between polymerization time and percentage of grafting of PMMA using 2 as initiator.

pose by the action of carboxyl groups on the surface.

Proof of Grafting from Carbon Black

The carbon black obtained from the polymerization produced a stable colloidal dispersion in a good solvent for PMMA. This suggests that PMMA is grafted from carbon black surface. Therefore, the percentage of grafting of PMMA was determined.

Figure 2 shows the relationship between polymerization time and percentage of grafting. The percentage of grafting increased to 40% with progress of polymerization, but no longer increased after 2 h. On the other hand, grafting efficiency (the proportion of grafted

polymer to total polymer formed) at 70 and 90°C was 62–70% and 46–53%, respectively.

These percentages of grafting and grafting efficiency are much larger than those obtained from the polymerization in the presence of carbon black using benzoyl peroxide as an initiator.¹³ This may be due to the fact that PMMA is propagated from the radical on the surface produced by the decomposition of peroxyester groups (eq 1).

Graft Polymerization of MMA Initiated by 3

The initiating activity of the graft polymerization of MMA for furnace black 3 was examined. The results are shown in Figure 3. As shown in Figure 3, 3 also has ability to initiate the polymerization of MMA. Although the rate of the polymerization initiated by 3 is somewhat less than that of 2, conversion increased to 11% after 6 h at 90°C.

As mentioned above, carboxyl groups accelerate the decomposition of peroxyester groups. Different from 2, carboxyl groups introduced onto furnace black were almost quantitatively transferred to acyl chloride groups by treatment with thionyl chloride for the introduction of peroxyester groups. The acyl chloride groups remaining unchanged during the reaction with *t*-BuOOH were treated with methanol to give methyl ester groups. Accordingly, the content of carboxyl groups of 3 is considered to be negligibly small.

Based on the above results, it is concluded that *tert*-butyl peroxyester groups on 3 decompose gradually and the polymerization proceeds to higher conversion.

Figure 4 shows the effects of the amount of carbon black 3 on the polymerization of MMA. The rate of the polymerization increased with increase of the amount of 3 as initiator.

The percentage of grafting of PMMA obtained from the polymerization initiated by 3 is shown in Figure 5. The percentage of grafting increased to 80% with progress of polymerization. This may be due to the propagation

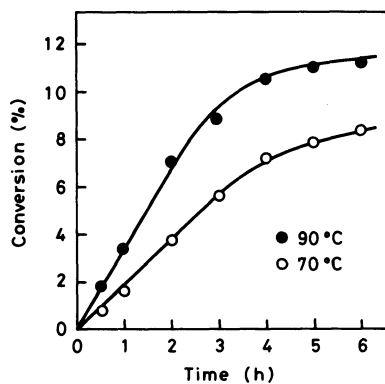


Figure 3. Graft polymerization of MMA initiated by 3. Polymerization conditions are given in Figure 1.

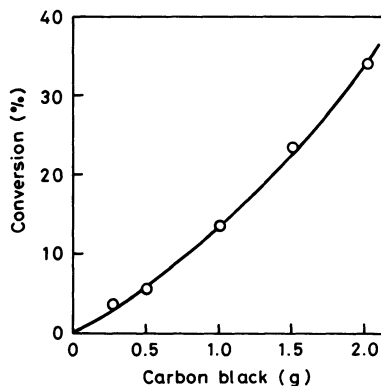


Figure 4. Effects of the amount of 3 on the graft polymerization of MMA. MMA, 10.0 ml; 70°C; 3 h.

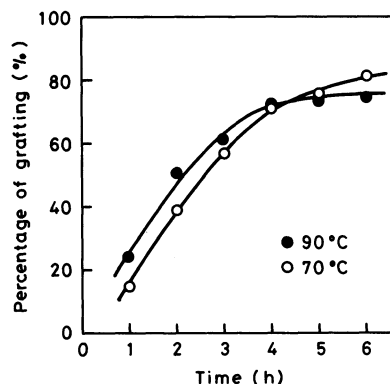


Figure 5. Relationship between polymerization time and percentage of grafting of PMMA using 3 as initiator.

of PMMA from the radical produced by the decomposition of peroxyester groups on 3. Therefore, it is apparent that PMMA is effec-

Table IV. Graft polymerization of several vinyl monomers initiated by **3**^a

Monomer	<i>e</i> -Value	Time	Conversion	Percentage of grafting
		h	%	%
Methyl methacrylate	0.400	6	8.4	81.5
Methyl acrylate	0.600	6	7.3	74.7
Acrylonitrile	1.200	12	4.2	18.9
Styrene	-0.800	12	trace	—
Vinyl acetate	-0.220	12	trace	—
<i>N</i> -Vinyl-2-pyrrolidone	-1.140	12	trace	—

^a Carbon black **3**, 0.50 g; monomer, 10.0 ml; 70°C.

tively grafted onto the surface by use of **3** as initiator.

Graft Polymerization of Several Vinyl Monomers

By use of **3** as initiator, the graft polymerizations of methyl acrylate, acrylonitrile, styrene, vinyl acetate, and *N*-vinyl-2-pyrrolidone were carried out and the polymerizability of these monomers was compared with MMA. The results are summarized in Table IV.

As shown in Table IV, it is apparent that **3** has ability to initiate the polymerization of vinyl monomers with positive *e*-value, such as MMA, methyl acrylate, and acrylonitrile, and the corresponding polymers are effectively grafted onto carbon black surface. However, the graft polymerization of vinyl monomers with negative *e*-value, such as styrene, vinyl acetate, and *N*-vinyl-2-pyrrolidone, were scarcely initiated by **3**.

In the previous paper, we reported that the radical polymerization of vinyl monomers with negative *e*-value in the presence of carbon black was remarkably retarded when peroxides such as benzoyl peroxide were used as initiators.^{13,14} Accordingly, it seems that the graft polymerization of vinyl monomers with negative *e*-value initiated by *tert*-butyl peroxyester groups on carbon black is completely retarded. This suggests that the radical graft polymerization from radical on carbon black is limited to vinyl monomers with positive *e*-

values.

Radical graft polymerization of vinyl monomers from carbon black initiated by carbon black having azo groups is now under investigation.

REFERENCES

1. N. Tsubokawa, A. Funaki, Y. Yamada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3297 (1982).
2. N. Tsubokawa, T. Ohyama, A. Yamada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 489 (1985).
3. N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1515 (1984).
4. N. Tsubokawa, *J. Polym. Sci., Part A, Polym. Chem.*, **25**, 1979 (1987).
5. G. Kraus and R. L. Collins, *Rubber World*, **139**, 219 (1958).
6. N. Tsubokawa, K. Fujiki, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 197 (1986); *J. Macromol. Sci. Chem.*, accepted for publication.
7. G. Smets, A. Poot, and G. L. Duncan, *J. Polym. Sci.*, **54**, 65 (1961).
8. T. Saegusa, M. Nozaki, and R. Noda, *Kogyo Kagaku Zasshi*, **57**, 249 (1954).
9. W. Hahm and A. Fisch, *Makromol. Chem.*, **16**, 36 (1955).
10. R. Yosomiya and T. Fujisawa, *Polym. Bull.*, **13**, 7 (1985).
11. K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and H. Eguchi, *Nippon Gomu Kyokaishi*, **49**, 900 (1976).
12. J. Volhard, *Justus Liebigs Ann. Chem.*, **190**, 40 (1878).
13. K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and N. Takashina, *Carbon*, **13**, 443 (1975).
14. N. Tsubokawa, H. Shirasaka, and Y. Sone, *Nippon Gomu Kyokaishi*, **58**, 26 (1985).