Polymer Journal, Vol. 27, No. 6, pp 623—630 (1995)

Grafting of Polymers onto Carbon Black Surface by the Trapping of Polymer Radicals Formed by the Decomposition of Peroxide Polymers

Shinji HAYASHI, Satoshi HANDA, Yoshihiro OSHIBE,*
Takashi YAMAMOTO,* and Norio TSUBOKAWA†

Department of Chemistry and Chemical Engineering, Faculty of Engineering,
Niigata University, 8050, Ikarashi 2-nocho, Niigata 950–21, Japan
** Chemicals and Explosive Laboratory, Nippon Oil and Fats Co.,*
Ltd., Taketoyo-cho, Chita-gun, Aichi 470–23, Japan

(Received December 13, 1994)

ABSTRACT: Grafting reaction of peroxide polymers having pendant peroxycarbonate groups with carbon black surface was investigated. Peroxide polymers having pendant peroxycarbonate groups were prepared by the photo copolymerization of vinyl monomers with *t*-butylperoxy-2-methacryloyloxyethylcarbonate (HEPO) using 2,2′-azobisisobutyronitrile at room temperature. The grafting reaction of carbon black with the peroxide polymers was carried out at 100—110°C with stirring under nitrogen. Even if polymer having no pendant peroxide groups was heated with carbon black, no grafting of polymers onto the surface was observed. On the contrary, by the heating of the peroxide polymers with carbon black in toluene, the corresponding polymers were grafted onto the surface: the percentage of poly(methyl methacrylate-*co*-HEPO) grafting onto furnace black was determined to be 27.9%. The percentage of grafting tends to increase with increasing HEPO content of the copolymer. Based on the above results, it is suggested that polymer radicals formed by the thermal decomposition of pendant peroxycarbonate groups are trapped by polycondensed aromatic rings of carbon black. The grafting method according to the radical trapping by carbon black surface is useful for the grafting of polymers onto carbon black having few functional groups, such as furnace and acetylene black. Polymer-grafted carbon black gave a stable colloidal dispersion in good solvents for grafted polymer.

KEY WORDS Surface Grafting of Polymer / Carbon Black / Peroxide Polymer / *t*-Butylperoxy-2-methacryloyloxyethylcarbonate / Vinyl Polymer / Radical Trapping / Dispersibility /

In a series of our papers, the grafting of polymers onto carbon black surface has been investigated by three methods: (a) Grafting *from* the surface; grafting of polymer chains are initiated from initiating groups introduced onto the surface, (b) grafting *onto* the surface; propagating polymer radicals are trapped by carbon black surface during the polymerization initiated by a conventional radical initiator in the presence of carbon black, and (c) grafting reaction of polymers with functional groups on the surface; polymers having terminal functional groups are reacted with functional groups on carbon black surface.[1-3] The methods (a) and (c) are unable to apply to the surface grafting of polymers onto furnace black and acetylene black, because these carbon blacks have few functional groups.

It is well known that polycondensed aromatic rings of carbon black act as a strong radical trapping agent.[4,5] We have reported that during the polymerization initiated by the

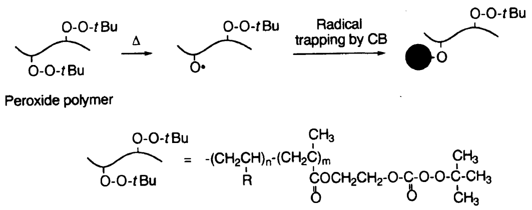
---

[†] To whom all correspondence should be addressed.

conventional radical initiators in the presence of carbon black, a part of polymer formed is grafted onto the surface, but the percentage of grafting is less than 10% because of preferential trapping of initiator fragments.[6,7]

Recently we have reported that polymer-grafted carbon black with considerably high percentage of grafting is obtained by the trapping of polymer radicals, which formed by the thermal decomposition of azo polymers[8] and peroxide polymers,[9] by aromatic rings of carbon black surface. Therefore, we pointed out that the grafting of polymers by the polymer radical trapping is very useful in the grafting of polymers onto carbon black surface having few functional groups.

In the present paper, the preparation of peroxide polymers having pendant peroxycarbonate groups and the grafting of polymers onto carbon black surface by the reaction of polymer radicals formed by the decomposition of the peroxide polymers with polycondensed aromatic rings of carbon black surface were investigated (Scheme 1).



Scheme 1.

EXPERIMENTAL

Materials

Carbon blacks used were furnace black Philblack O and Philblack I (Phillips Petroleum Co.), channel black Neospectra II (Columbian Carbon Corp.), and acetylene black Denkablack (Denki Kagaku Kogyo Co., Ltd.). Furnace blacks were extracted with chloroform to remove resinous substances. Neospectra II and Denkablack were used without further purification. These carbon blacks were dried *in vacuo* at 120°C before use. The properties of these carbon blacks are shown in Table I.

Methyl methacrylate (MMA) was washed with dilute aqueous solution of sodium hydrogen sulfite, dried over sodium sulfate, and distilled under reduced pressure. Styrene (St) was washed with aqueous alkali, dried over calcium chloride, and distilled under reduced pressure. Vinyl acetate (VAc) was purified by distillation before use. *t*-Butylperoxy-2-methacryloyloxyethylcarbonate (HEPO), obtained from Nippon Oil and Fats Co., Ltd., Japan, was used without further purification. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Toluene was washed with H_2SO_4 and aqueous alkali, dried over calcium chloride, refluxed over sodium, and distilled.

Preparation and Characterization of Peroxide Polymers

Peroxide polymers were prepared by copolymerization of vinyl monomers with HEPO.[10] A typical example was as follows. Into a flask,

Table I. Properties of carbon blacks

Carbon black	Surface area	Particle size	Functional group/mmol g^{-1}		
	$m^2 g^{-1}$	nm	Phenolic hydroxyl	Quinonic oxygen	Carboxyl
Philblack O[a]	79.6	29.4	0.02	0.18	0
Philblack I[a]	116.8	28	0.05	0.23	0
Neospectra II[b]	906	13	0.24	0.92	0.40
Denkablack[c]	65.0	40	0.02	0.01	0

[a] Furnace black. [b] Channel black. [c] Acetylene black.

50 mL of toluene, 103 mL of St, 24.6 g of HEPO and 0.50 g of AIBN were charged under dry nitrogen. The reaction mixture was irradiated with a 100 W high pressure UV lamp under stirring with a magnetic stirrer at a constant rate at room temperature. After the reaction, the product was poured into a large excess of methanol. The peroxide polymers thus obtained were purified by reprecipitation and stored in the dark below $-30^{\circ}C$.

The structure of copolymers was identified by IR spectra. The molecular weight of peroxide polymer was determined by GPC using polystyrene standards. The monomer composition of copolymer was determined by ^1H NMR and elemental analysis. The content of peroxide groups in the copolymer was determined by iodometry according to the method of literatures.[10,11]

Grafting Reaction of Peroxide Polymers with Carbon Black

Into a flask, 0.30 g of carbon black, 1.0 g of peroxide polymer and 20.0 mL of toluene were charged and the reaction mixture was heated under stirring with a magnetic stirrer under nitrogen. After the reaction, the reaction mixture was poured into a large excess of methanol to precipitate the polymer-grafted carbon black.

Percentage of Grafting and Number of Grafted Polymer (Gn)

To remove ungrafted polymer, the product was dispersed in a good solvent for the polymer and the dispersion was centrifuged at 1.2×10^4 rpm. Thus, the procedures were repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting and the number of grafted polymer (*Gn*) were calculated by the following equations.

$$\text{Grafting (\%)} = \frac{A}{B} \times 100$$

$$Gn\,(\text{No.}\,\text{g}^{-1}) = 6.02 \times 10^{23} \times \frac{A/M_n}{B}$$

A, polymer grafted (g); B, carbon black charged (g); M_n, molecular weight of grafted polymer

Stability of Polymer-Grafted Carbon Black Dispersion

The stability of polymer-grafted carbon black dispersion in tetrahydrofuran (THF) was estimated from the carbon black content in the dispersion after standing at room temperature. The detailed procedures were described in the previous paper.[12]

RESULTS AND DISCUSSION

Preparation of Peroxide Polymers

In our previous paper, we reported the preparation of peroxide polymers having benzoyl peroxide groups in the main chain by the cationic polymerization of styrene and ring-opening polymerization of THF and ε-caprolactone in the presence of 3,3′-bis(chloromethyl)benzoyl peroxide diperchlorate which was prepared by the reaction of 3,3′-bis(chloromethyl)benzoyl peroxide with silver perchlorate.[9] These peroxide polymers were readily decomposed in the presence of carbon black and polymer radicals formed were successfully trapped by carbon black surface.

On the other hand, we have also reported that polymers having pendant peroxycarbonate groups are readily prepared by the copolymerization of vinyl monomers with HEPO and these peroxide polymers have an ability to initiate the radical polymerization of vinyl monomers to give block copolymers.[10,13]

Therefore, to apply such peroxide polymer for the surface grafting of polymers onto carbon black surface, the photo copolymerization of HEPO with vinyl monomers such as MMA, St, and VAc initiated by azo initiator at room temperature was investigated. The results are shown in Table II.

Table II. Properties of peroxide polymer

Peroxide polymer	HEPO in feed	HEPO content in copolymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
	wt%	mol%	$\times 10^3$	
Poly(MMA-*co*-HEPO) **1**	1.0	4.0	7.5	2.32
Poly(MMA-*co*-HEPO) **2**	2.0	6.0	6.8	2.30
Poly(MMA-*co*-HEPO) **3**	4.0	8.0	7.0	2.32
Poly(MMA-*co*-HEPO) **4**	9.0	10.0	6.9	2.32
Poly(St-*co*-HEPO)	10.0	10.0	9.6	2.03
Poly(VAc-*co*-HEPO)	10.0	8.0	29.8	1.62

Table III. Grafting reaction of poly(MMA-*co*-HEPO) with Philblack O[a]

Peroxide polymer	Temperature	Grafting	*Gn*[b]
	°C	%	$\times 10^{19}$ No. g^{-1}
PMMA	100	9.7	—
Poly(MMA-*co*-HEPO) **1**	30	9.0	—
Poly(MMA-*co*-HEPO) **1**	100	17.8	1.43
Poly(MMA-*co*-HEPO) **2**	100	18.6	1.65
Poly(MMA-*co*-HEPO) **3**	100	22.9	1.97
Poly(MMA-*co*-HEPO) **4**	100	27.9	2.43

[a] Philblack O, 0.30 g; polymer, 1.00 g; toluene, 20.0 mL; 4 h. [b] Number of grafted polymer.

As shown in Table II, HEPO content of peroxide polymers, *i.e.*, poly(MMA-*co*-HEPO), poly(St-*co*-HEPO), and poly(VAc-*co*-HEPO), was almost equal to those of monomer feed. The pendant peroxycarbonate groups were confirmed to be remaining undecomposed by titration. This is due to the fact that the decomposition rate of pendant peroxycarbonate groups was negligibly small at room temperature.[10,13]

Grafting Reaction of Poly(MMA-co-HEPO) onto Carbon Black Surface

In the previous paper, we have reported that polymer radicals formed by decomposition of azo polymers[8] and peroxide polymers[9] are effectively trapped by polycondensed aromatic rings of carbon black surface to give the corresponding polymer-grafted carbon black. Therefore, the grafting reaction of peroxide polymer having pendant peroxycarbonate groups with carbon black surface was examined.

Table III shows the results of the grafting reaction of peroxide polymers, poly(MMA-*co*-HEPO)s, having different HEPO composition, with furnace black Philblack O. When PMMA having no peroxide groups was heated with Philblack O in toluene, PMMA retained by carbon black surface after Soxhlet extraction with THF was less than 10%; this may be due to physical adsorption of PMMA by carbon black. When poly(MMA-*co*-HEPO) was reacted with carbon black at 30.0°C, at which the decomposition of pendant peroxycarbonate groups is negligibly small, the amount of PMMA retained by carbon black after the reaction was almost equal to that adsorbed. Therefore, the grafting reaction was found to scarcely proceed at the temperature.

On the contrary, it was found that the corresponding copolymers are grafted onto the surface by the heating of poly(MMA-*co*-HEPO)s with Philblack O at 100°C; the

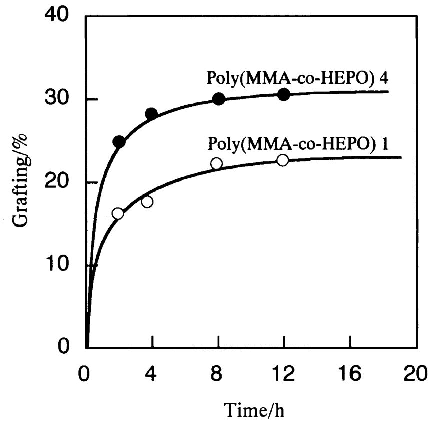


Figure 1. Grafting reaction of poly(MMA-*co*-HEPO) with carbon black. Philblack O, 0.30 g; peroxide polymer, 1.00 g; toluene, 20.0 mL; 110°C.

percentage of grafting onto carbon black surface was 18—28%. The percentage of grafting and the number of grafted polymer chains (*Gn*) increased with increasing HEPO content of the peroxide polymers.

Figure 1 shows the relationship between percentage of grafting of PMMA and reaction time in the reaction of poly(MMA-*co*-HEPO) **1** and **4** at 110°C. The percentage of grafting increased with progress of the reaction and no longer increased after 8 h. This suggests that the reaction of polymer radicals with carbon black is hindered by previously grafted polymer chains on the surface at the last stage of the reaction. Figure 1 also shows that the percentage of grafting of poly(MMA-*co*-HEPO) **4** is larger than that of poly(MMA-*co*-HEPO) **1**, because of higher HEPO content of the copolymers.

Table IV shows the results of the grafting reaction of poly(MMA-*co*-HEPO)s with channel black Neospectra II. These copolymers were found to be also grafted onto Neospectra II by use of the corresponding peroxide polymers. The percentage of grafting tends to increase with increasing HEPO content of the peroxide polymers, but the percentage of grafting of poly(MMA-*co*-HEPO)s **3** and **4** became almost equal. This suggests that the percentage of grafting of the peroxide polymers onto Neopsectra II does not exceed about 30%, because of blocking effect of previously grafted polymer and steric hindrance of carbon black surface.

Table IV. Grafting reaction of poly(MMA-*co*-HEPO) with Neospectra II[a]

Peroxide polymer	Grafting	*Gn*[b]
	%	$\times 10^{19}$ No. g^{-1}
Poly(MMA-*co*-HEPO) **1**	22.6	1.81
Poly(MMA-*co*-HEPO) **2**	24.6	2.18
Poly(MMA-*co*-HEPO) **3**	30.2	2.59
Poly(MMA-*co*-HEPO) **4**	28.9	2.52

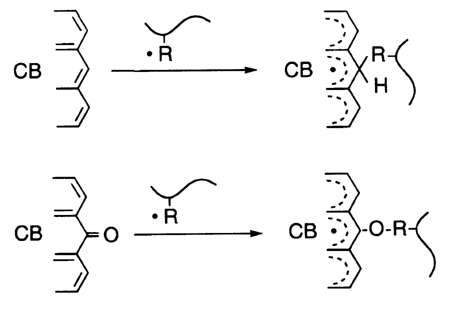
[a] Neospectra II, 0.30 g; polymer, 1.00 g; toluene, 20.0 mL; 100°C; 12 h. [b] Number of grafted polymer.

Mechanism of Grafting

Based on the above results, it is concluded that polymer radicals formed by the thermal decomposition of pendant peroxycarbonate groups of poly(MMA-*co*-HEPO)s are successfully captured by carbon black surface.

As mentioned above, it is well known that carbon blacks act as a strong radical scavenger.[4,5] When carbon blacks were treated with a conventional radical initiator such as benzoyl peroxide and 2,2′-azobis(isobutyronitrile), the corresponding radicals are bonded onto the surface by addition reaction with polycondensed aromatic rings and quinonic oxygen groups on the surface.[14,15] The free radicals formed on carbon black surface by the addition of initiator radicals were considered to be stabilized by polycondensed aromatic rings: the increase of surface radicals after the treatment with the radical initiators has been confirmed by ESR.[16]

Therefore, polymer radicals were considered to be bonded to polycondensed aromatic rings by addition of polymer radicals as shown in Scheme 2. It seems that quinonic oxygen groups on the surface also act as trapping sites of polymer radicals, especially in the reaction with



Scheme 2.

channel black having much quinonic oxygen groups.

Effect of Temperature on the Grafting Reaction

We also investigated the effect of temperature on the grafting reaction of poly(MMA-*co*-HEPO) **3** with carbon black. The results are shown in Figure 2. The percentage of grafting increased with increasing reaction temperature and was about constant above 100°C. The result indicates that the decomposition of pendant peroxycarbonate groups of poly(MMA-*co*-HEPO) was accelerated at higher temperature, but no longer increased above 100°C; this temperature is close to temperature giving a 10 h half-life of HEPO.[11] Accordingly, the result indicates that large excess of polymer radicals are reacted with carbon black surface above 100°C.

Grafting Reaction of Various Peroxide Polymers with Carbon Blacks

Table V shows the result of grafting reaction of various carbon blacks with poly(MMA-*co*-HEPO) **3**, poly(St-*co*-HEPO), and poly(VAc-*co*-HEPO). It became apparent that by use of peroxide polymers having pendant peroxycarbonate groups, the corresponding polymers are effectively grafted onto the surface. The percentage of grafting onto carbon black obtained from the reaction with poly(VAc-*co*-HEPO) having the highest molecular weight was larger than that from the reaction with poly(MMA-*co*-HEPO) and poly(St-*co*-HEPO), but the number of grafted polymer chains (*Gn*) was smallest. This may be due to carbon black surface being shielded by neighboring grafted chains. This effect on the grafting reaction was enhanced with increasing molecular weight of peroxide polymers.

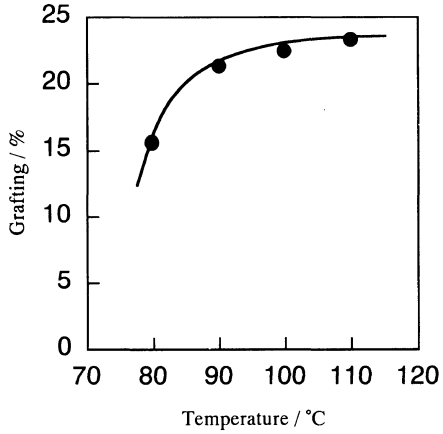


Figure 2. Effect of temperature on the grafting reaction of poly(MMA-*co*-HEPO) **3** with carbon black. Philblack O, 0.30 g; peroxide polymer, 1.00 g; toluene, 20.0 mL; 10 h.

The percentage of grafting of peroxide polymers onto Neospectra II was larger than that of Philblack O and Denkablack. This may be due to the higher content of quinonic oxygen groups and the larger surface area.

As mentioned above, the effective grafting of polymers onto furnace and acetylene black, such as Philblack O and Denkablack having few functional groups, has been difficult by the conventional methods.[1-3] On the contrary, the grafting method according to the radical trapping by polycondensed aromatic rings of carbon black surface was found to be very useful for the grafting of polymers onto carbon black having few functional groups, such as furnace and acetylene black.

Dispersibility of Polymer-Grafted Carbon Black

The stability of dispersion of poly(MMA-*co*-HEPO)-grafted carbon black (grafting = 27.9%; $Gn = 2.4 \times 10^{19}$) and poly(VAc-*co*-HEPO)-grafted carbon black (grafting 49.7%;

Table V. Grafting reaction of peroxide polymers with various carbon blacks[a]

Carbon black	Peroxide polymer	Grafting %	Gn[b] $\times 10^{19}$ No. g^{-1}
Neospectra II	Poly(MMA-*co*-HEPO) 3	30.2	2.59
Philblack O	Poly(MMA-*co*-HEPO) 3	28.3	2.43
Philblack I	Poly(MMA-*co*-HEPO) 3	21.8	1.87
Denkablack	Poly(MMA-*co*-HEPO) 3	20.9	1.80
Neospectra II	Poly(St-*co*-HEPO)	51.6	3.24
Philblack O	Poly(St-*co*-HEPO)	29.8	1.87
Philblack I	Poly(St-*co*-HEPO)	26.0	1.63
Denkablack	Poly(St-*co*-HEPO)	21.5	1.35
Neospectra II	Poly(VAc-*co*-HEPO)	88.2	1.78
Philblack O	Poly(VAc-*co*-HEPO)	49.7	1.01
Philblack I	Poly(VAc-*co*-HEPO)	48.7	0.98
Denkablack	Poly(VAc-*co*-HEPO)	40.4	0.82

[a] CB, 0.60 g; polymer, 2.00 g; toluene, 40.0 mL; 100°C; 10 h. [b] Number of grafted polymer.

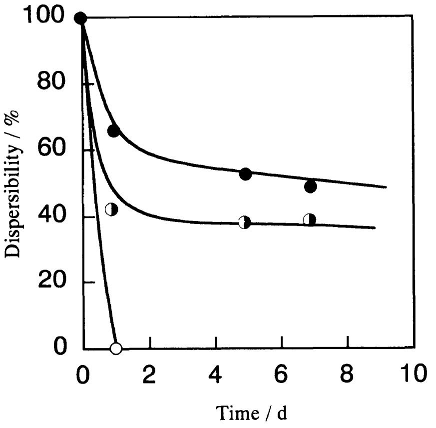


Figure 3. Stability of polymer-grafted carbon black dispersion in THF at room temperature. (○), ungrafted carbon black; (●), poly(MMA-*co*-HEPO)-grafted carbon black (grafting = 27.9%; $Gn = 2.4 \times 10^{19}$); (◑), poly(VAc-*co*-HEPO)-grafted carbon black (grafting = 49.7%; $Gn = 1.0 \times 10^{19}$).

$Gn = 1.0 \times 10^{19}$) was compared with that of untreated carbon black. The results are shown in Figure 3. It was found that the dispersibility of carbon black was remarkably improved by the grafting of polymers onto the surface. This suggests that grafted polymer chains on carbon black surface interfere with the aggregation of carbon black particles.

In spite of lower grafting, the dispersion of poly(MMA-*co*-HEPO)-grafted carbon black was more stable than that of poly(VAc-*co*-HEPO)-grafted carbon black. These results suggests that the dispersibility of polymer grafted carbon black was affected by the number of grafted chain rather than percentage of grafting.

CONCLUSIONS

1. Peroxide polymers were readily prepared by the photo copolymerization of various vinyl monomers with HEPO using azo initiator at room temperature.
2. By the reaction of carbon black with peroxide polymers in toluene, polymer radicals formed by decomposition of the pendant peroxycarbonate groups of peroxide polymers were trapped by carbon black surface to give the corresponding polymer-grafted carbon black.
3. Polymer-grafted carbon black thus obtained gave a stable colloidal dispersion in solvents for grafted polymer chain.

REFERENCES

1. N. Tsubokawa, *Hyomen*, **28**, 286 (1990).
2. N. Tsubokawa, *J. Jpn. Soc. Color Material*, **65**, 72

(1992).
3. N. Tsubokawa, *Prog. Polym. Sci.*, **17**, 417 (1992).
4. M. Levy and M. Szwarz, *J. Chem. Phys.*, **22**, 1621 (1954).
5. D. Hey and G. Williams, *Discuss. Faraday Soc.*, **14**, 216 (1953).
6. K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and N. Takashina, *Carbon*, **13**, 443 (1975).
7. K. Ohkita, N. Tsubokawa, and E. Saitoh, *Carbon*, **16**, 41 (1978).
8. N. Tsubokawa and K. Yanadori, *Kobunshi Ronbunshu*, **49**, 865 (1992).
9. N. Tsubokawa and S. Handa, *J. Jpn. Soc. Color Material*, **66**, 468 (1993).
10. K. Nozaki, *Ind. Eng. Chem. Anal. Ed.*, **18**, 583 (1964).
11. T. Yamamoto, K. Aoshima, H. Ohmura, Y. Moriya, N. Suzuki, and Y. Oshibe, *Polymer*, **32**, 19 (1991).
12. N. Tsubokawa and M. Hosoya, *Reactive Polym.*, **14**, 33 (1991).
13. T. Yamamoto, H. Ohmura, Y. Mori, N. Suzuki, Y. Oshibe, and M. Sugiura, *Nippon Kagaku Kaishi*, 1269 (1992).
14. J. B. Donnet, G. Henrich, and L. Geidreich, *Compt. Rend.*, **249**, 97 (1959).
15. K. Ohkita, H. Kasahara, N. Ishizuke, and Y. Itagaki, *Nippon Gomu Kyokaishi*, **30**, 36 (1963).
16. J. W. C. Spackman, *Chem. Ind.* (*London*), 1532 (1961).