

Grafting of Polymers onto a Carbon Black Surface by the Trapping of Polymer Radicals

Shinji Hayashi,¹ Atsushi Naitoh,¹ Seiichi Machida,¹ Masaki Okazaki,¹ Kiyotaka Maruyama¹ and Norio Tsubokawa^{2*}

¹Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

²Department of Material Science and Technology, Faculty of Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

The grafting of polymers onto a carbon black surface based on the trapping of polymer radicals by polycondensed aromatic rings of the surface was investigated. It was found that polymer radicals formed by the thermal decomposition of azo-polymer, peroxy-polymer and 2,2,6,6-tetramethylpiperidiny-1-oxy-terminated polymer are successfully captured by a carbon black surface to give the corresponding polymer-grafted carbon blacks. The grafting of polymers onto carbon black was also achieved by the trapping of polymer radicals formed by the redox reaction of ceric ions with polymers having hydroxyl groups. It was concluded that surface grafting of polymers onto carbon black is effective when there are few functional groups. The electrical resistance of poly(ethylene oxide) (PEO)-grafted carbon black thus obtained is increased drastically to about 10^4 – 10^5 times the initial resistance at the melting point of PEO. This may be due to a widening of the gaps between the carbon black particles by melting of PEO. In addition, it was found that the electrical resistance of a crystalline poly(ethylene imine) (PEI)-grafted carbon black drastically increased to 10^3 – 10^4 times the initial resistance in methanol, ethanol and water vapor, but hardly any change in electrical resistance was observed in n-hexane or toluene vapor. These results suggest the possibility of detecting a slight change in the crystalline structure of PEI upon absorption of solvent vapor as a large increase in the electrical resistance of the polymer-grafted carbon black.

© 1998 John Wiley & Sons, Ltd.

Keywords: carbon black; surface grafting of polymer; polymer radical; radical trapping;

azo-polymer; peroxy-polymer; electrical resistance; poly(ethylene oxide); poly(ethylene imine)

Received 17 June 1997; accepted 18 November 1997

INTRODUCTION

In a series of papers, we have reported the grafting of polymers onto a carbon black surface by the following 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) polymer reactions with functional groups on the surface—polymers having terminal functional groups are reacted with functional groups on the carbon black surface.^{1–3}

The radical, cationic and anionic polymerization initiated by azo-⁴ or peroxyester,⁵ acylium perchlorate⁶ and potassium carboxylate groups⁷ introduced onto a carbon black surface are examples of method (a). An important characteristic of method (c) is the fact that not only the molecular weight and the number of grafted polymers on the carbon black surface are easily controlled, but also a polymer with a well-defined structure can be grafted.⁸ Methods (a) and (c), however, cannot be applied 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 the polycondensed aromatic rings of carbon black act as a strong radical-trapping agent.^{9,10} We have reported that during polymerization initiated by the conventional radical initiators in the presence of carbon black, i.e.

* Correspondence to: Norio Tsubokawa, Department of Material Science and Technology, Faculty of Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan.

method (c), part of the polymer formed is grafted onto the surface, but the percentage of grafting is less than 10%, because carbon black traps more low-molecular-weight initiator fragments than growing polymer radicals.^{11,12} It is expected, therefore, that effective grafting of polymers onto the surface will be achieved if the reaction of carbon black with polymer radicals is conducted in the absence of low-molecular-weight fragment radicals.

In the present work, the grafting of polymers onto a carbon black surface by trapping polymer radicals formed by the thermal decomposition of azo polymers, peroxy polymers and 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO)-terminated polymers was investigated (Schemes 1,2,3, below.) In addition, the reaction of a carbon black surface with polymer radicals formed by the redox reaction of ceric ions with polymers having hydroxyl groups was examined (Scheme 4 below). The electrical properties of polymer-grafted carbon black will be discussed.

EXPERIMENTAL

Carbon blacks and reagents

The carbon blacks used were furnace black Philblack O (BET surface area $79.6 \text{ m}^2 \text{ g}^{-1}$) and Philblack I ($116.8 \text{ m}^2 \text{ g}^{-1}$) obtained from Phillips Petroleum Co. Azo polymers were prepared by the polycondensation of 4,4'-azobis(4-cyanopentanoyl dichloride) with polymers having terminal hydroxyl or amino groups, such as poly(ethylene oxide) (PEO), poly(dimethylsiloxane) (PDS), and poly(ethylene imine) (PEI).^{13,14} Peroxy polymers were prepared by the cationic polymerization of styrene and ring-opening polymerization of tetrahydrofuran (THF) and ϵ -caprolactone (CL) using 3,3'-bis-(chloromethyl)benzoyl peroxide diperchlorate as an initiator.¹⁵ TEMPO-terminated polystyrene was prepared according to the literature method.^{16,17}

Grafting reaction and determination of percentage of grafting

The grafting reaction was conducted in a 100 ml flask under nitrogen and stirred with a magnetic stirrer. The detailed procedures were described previously.^{14,15} The isolation of polymer-grafted carbon black from ungrafted polymer was carried as follows: the reaction product was dispersed in a

Table 1 Grafting of polymer onto carbon black by reaction with azo polymer^a

Azo polymer	$\bar{M}_n \times 10^{-3}$	Temperature (°C)	Grafting (%)
PDS	4.5	40	9.2
PDS	4.5	70	42.1
PDS	9.6	70	30.5
PEO	4.0	70	35.7
PEI	4.8	70	20.4

^a Carbon black (Philblack I), 0.30 g; polymer, 5.0 g; toluene, 20.0 ml; 24 h.

good solvent of the grafted polymer and the dispersion was centrifuged. The supernatant solution was removed by decantation and the precipitated carbon black was dispersed in solvent. The centrifugation was repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting was determined by Eqn [1]. The amount of polymer grafted onto the carbon black A (g), was determined from the weight loss when B g of polymer-grafted carbon black was heated at 500 °C by a thermal analyzer.

$$\text{Grafting (\%)} = (A/B - A) \times 100 \quad [1]$$

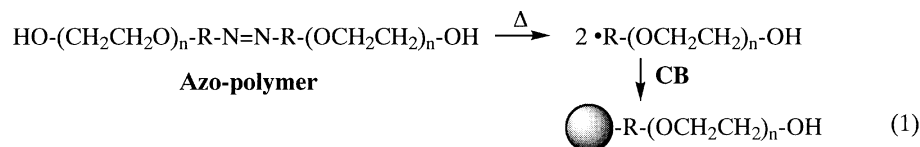
Electrical resistance of polymer-grafted carbon black

The procedure for the measurement of electrical resistance of polymer-grafted carbon black under various conditions was described in detail previously.¹⁸

RESULTS AND DISCUSSION

Trapping of polymer radicals formed by decomposition of azo-polymer and peroxy polymer

In general, polymers having azo bonds in the main chain, i.e. azo-polymers, are used for the preparation of block copolymers by radical polymerization of vinyl monomers.¹³ The grafting of polymers by the reaction of carbon black with polymer radicals formed by the thermal decomposition of azo-polymers was therefore investigated. As shown in Table 1, when these azo-polymers reacted with carbon black below 40 °C, the grafting of the polymer onto carbon black scarcely proceeded at



Scheme 1 Surface grafting onto carbon black by trapping polymer radicals formed by decomposition of azo-polymer.

Table 2 Grafting of polymers by the reaction with peroxy-polymers^a

Peroxy-polymer	$\bar{M}_n \times 10^{-3}$	Temperature (°C)	Grafting (%)
Polystyrene	5.5	30	18.6
Polystyrene	5.5	50	66.2
Polystyrene	5.5	70	68.1
PolyTHF	2.4	50	60.3
PolyCL	16.8	50	42.3

^a Carbon black (Philblack O), 0.30 g; polymer, 1.0 g; toluene, 20.0 ml; 48 h.

all, because the decomposition of the azo-polymer was very slow at that temperature. In contrast, above 70 °C the grafting reaction of these azo-polymers took place and the corresponding polymer-grafted carbon blacks were obtained. In addition, IR spectra of PEI-grafted carbon black, for example, shows new absorptions which are characteristic of PEI. The results indicate that the polymer radicals formed by the thermal decomposition of azo-polymer are effectively captured by the carbon black surface, as shown in Scheme 1.

Table 2 shows the result of the grafting reaction of peroxy-polymers with carbon black. It was found that these peroxy-polymers were readily decomposed in the presence of carbon black, and the polymer radicals formed were successfully trapped by the carbon black surface (Scheme 2). The grafting of polymers onto the carbon black surface was also confirmed by the IR spectra of polymer-grafted carbon black.

It is interesting to note that the the grafting

reaction proceeds even at 30 °C. This may be due to the fact that peroxide decomposes even at room temperature in the presence of carbon black.¹⁹

Trapping of polymer radicals formed by decomposition of TEMPO-terminated polystyrene

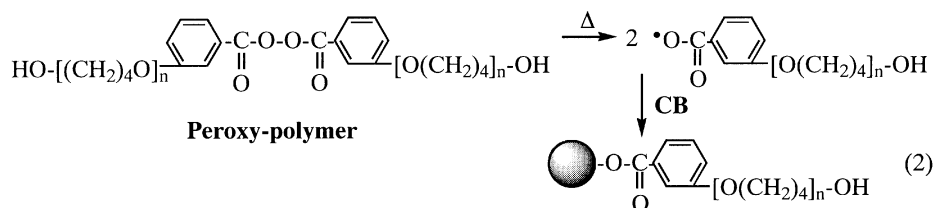
It has been reported that the use of TEMPO-based initiators, or systems containing TEMPO, for the free-radical polymerization of styrene result in a 'living' process.^{16,17} In addition, TEMPO-terminated polystyrene (TEMPO-PolySt) thus obtained has an ability to initiate the radical polymerization of vinyl monomers to give the corresponding block copolymer, because of the formation of polystyryl radicals resulting from the thermal decomposition of C–O–N bonds of TEMPO-PolySt.¹⁷

In the present work, the grafting reaction of carbon black with TEMPO-PolySt obtained from the above polymerization was examined. The

Table 3 Grafting of polymer onto carbon black by the reaction with TEMPO-PolySt^a

Polymer	$\bar{M}_n \times 10^{-3}$	Temperature (°C)	Grafting (%)
PolySt	11.4	125	5.0
TEMPO-PolySt	11.2	125	9.2
TEMPO-PolySt	3.2	80	4.8
TEMPO-PolySt	3.2	125	16.0
TEMPO-PolySt	3.2	135	17.5

^a Carbon black (Philblack I), 0.10 g; polymer, 1.0 g; *m*-xylene, 10.0 ml; 12 h.



Scheme 2 Surface grafting onto carbon black by trapping polymer radicals formed by decomposition of peroxy-polymer.

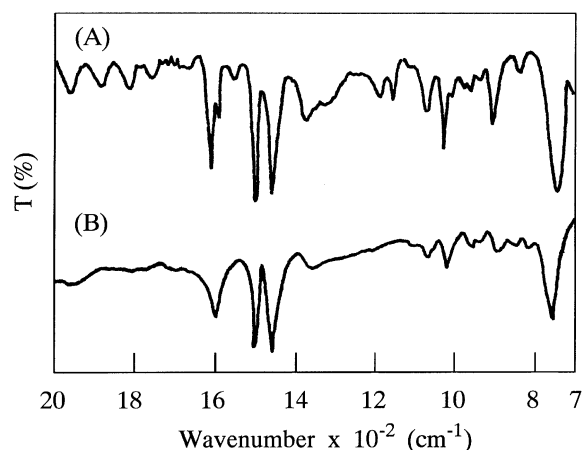
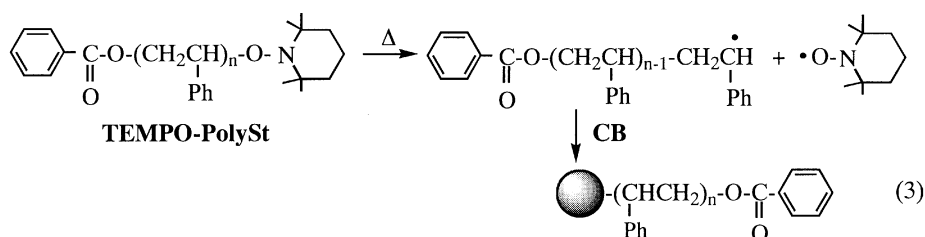


Figure 1 IR spectra of (A) polystyrene and (B) polystyrene-grafted carbon black.

results are shown in Table 3. No grafting of polystyrene was observed when the reaction was carried out below 80 °C, at which temperature there is scarcely any decomposition of C–O–N bonds. On the contrary, the grafting of polystyrene onto carbon black proceeded successfully above 100 °C.

Figure 1 shows IR spectra of polystyrene and polystyrene-grafted carbon black obtained from the reaction. It became apparent that the IR spectra of polystyrene-grafted carbon black shows new absorptions, which are characteristic of polystyrene. These results indicate that the polystyryl radicals formed by the decomposition of TEMPO-PolySt are trapped by the carbon black surface, as shown in Scheme 3. In the reaction system, the trapping of TEMPO by the carbon black surface was scarcely observed, because of the stability and the steric hindrance of the radical.



Scheme 3 Surface grafting onto carbon black by trapping polymer radicals formed by decomposition of TEMPO-PolySt.

Table 4 Grafting of carbon black with polymer radicals formed by redox reaction with Ce(IV)^a

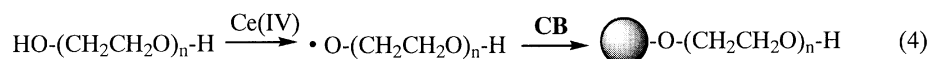
Polymer	$\bar{M}_n \times 10^{-3}$	Time (h)	Grafting (%)
PEO	3.0	12	49.7
PEO	8.0	12	57.5
PEO	20.0	12	56.5
PVA	22.0	12	33.5
Soluble starch	—	6	54.4

^a Carbon black (Philblack D), 0.30 g; polymer, 1.0 g; Ce(IV) soln., 1.0 ml; 25 °C.

Trapping of polymer radicals formed by redox reaction of ceric ions with polymers having hydroxyl groups

It has been reported that the radical polymerization of vinyl monomers is initiated by radicals formed by redox reaction of ceric ions with reducing agents such as alcohols, aldehydes and acids.²⁰ Particularly, a system consisting of ceric ions and alcohols has been applied to the grafting of vinyl monomers onto poly(vinyl alcohol) (PVA) and cellulose.²¹ It is therefore expected that polymer radicals formed by the redox reaction of ceric ions with polymers having hydroxyl groups are trapped by the carbon black surface to give the corresponding polymer-grafted carbon black.

For this paper, the grafting of polymers by the above system was investigated. Table 4 shows the results of the grafting reaction of diol-type PEO, PVA and soluble starch in the presence of ceric ions. In the absence of ceric ions no grafting of these polymers onto the surface was observed. In contrast, in the presence of ceric ions the corresponding polymers were effectively grafted onto the carbon black surface, as shown in Scheme 4. No gelation of polymers was observed in the reaction system. This indicates that radicals formed on the grafted chain on the carbon black surface hardly



Scheme 4 Surface grafting onto carbon black by trapping polymer radicals formed by redox reaction of ceric ions with polymer containing hydroxyl groups.

react with other carbon black particles, because the grafted polymer chain is fixed on the surface.

Grafting mechanism

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.^{22,23} The free radicals formed on the carbon black surface by the addition of initiator radicals were considered to be stabilized by polycondensed aromatic rings: the increase in surface radicals after the treatment with the radical initiators has been confirmed by ESR.²⁴

Grafted polymer were therefore considered to be bonded to polycondensed aromatic rings by addition of polymer radicals. It seems that quinonic oxygen groups on the surface also act as trapping sites for polymer radicals, especially in the case of the reaction with channel black, which has many quinonic oxygen groups.

Electrical properties of polymer-grafted carbon black

It has been reported that vinyl polymer-grafted carbon black, which was crosslinked with a variety of crosslinking agents, shows a positive temperature coefficient of resistance (PTC) near the glass transition temperature of the grafted polymer.^{25,26}

The effect of temperature on the electrical resistance of crystalline polymer-grafted carbon black was investigated. Figure 2 shows the relationship between temperature and electrical resistance of PEO-grafted carbon black prepared by the radical-trapping method. The electrical resistance of the PEO-grafted carbon black increased dramatically to about 10^4 – 10^5 times the initial resistance at the melting point of PEO. This may be due to a widening of the gaps between the carbon black particles by melting of the PEO.

We have already pointed out that the electrical resistance of a crystalline PEI-grafted carbon black

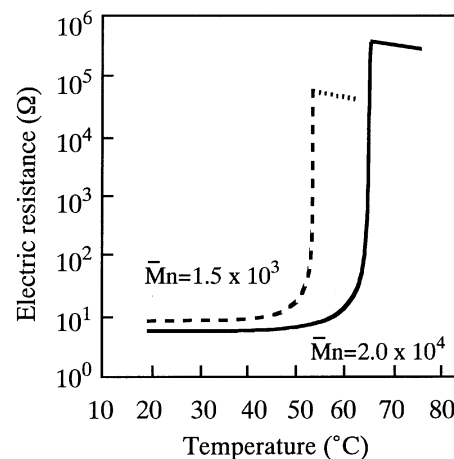


Figure 2 Effects of temperature on the electrical resistance of PEO-grafted carbon black.

increased dramatically to 10^3 – 10^4 times the initial resistance in methanol, ethanol and water vapor.¹⁸

In the present paper, the effects of methanol, water and n-hexane vapor on the electrical resistance of PEO-grafted carbon black were investi-

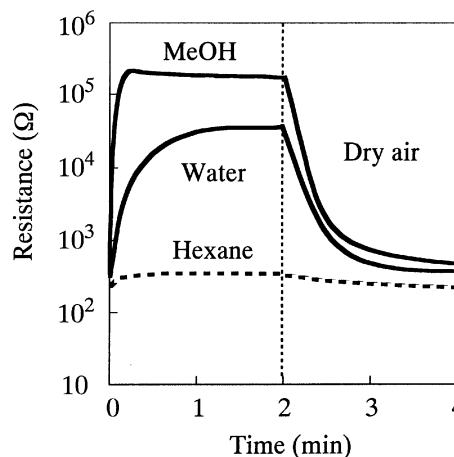


Figure 3 Effects of various vapors on the electrical resistance of crystalline PEO-grafted carbon black at 25 °C.

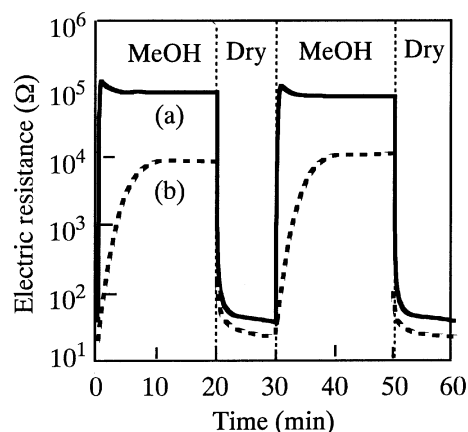


Figure 4 Responsiveness of the electrical resistance of crystalline PEI-grafted carbon black to methanol vapor at 25 °C. Carbon black content: (a) 10 wt%; (b) 20 wt%.

gated. Figure 3 shows the results. It became apparent that the electrical resistance of PEO-grafted carbon black increased to 10^2 – 10^3 times the initial resistance in methanol and water vapor, which are good solvents for PEO, but a change in electrical resistance of the composite was hardly observed in n-hexane vapor, which is a nonsolvent of PEO.

These results suggest the possibility of detecting a slight change in the crystalline structure of PEO by the absorption of solvent vapor as a large increase in the electrical resistance of the composite.

Figure 4 shows that the electrical resistance of PEI-grafted carbon black returned immediately to the initial resistance value when the composite was transferred to dry air. The responsiveness of the electrical resistance was reproducible even after 30 cycles of exposure to methanol vapor and dry air.

CONCLUSIONS

Polymer radicals, which were formed not only by the thermal decomposition of azo polymer, peroxy polymer and TEMPO-PolySt but also by the redox reaction of ceric ions with polymer having hydroxyl groups, were successfully trapped by a carbon black surface to give the corresponding polymer-grafted carbon black.

The grafting of PEO, PVA and soluble starch

onto carbon black was achieved by trapping the polymer radicals formed by redox reaction of ceric ions with these polymers.

The electrical resistance of PEO-grafted and PEI-grafted carbon black was found to respond to temperature and various vapors.

REFERENCES

1. N. Tsubokawa, *Prog. Polym. Sci.* **17**, 417 (1992).
2. N. Tsubokawa, *Kobunshi (High Polymer)* **45**, 412 (1966).
3. N. Tsubokawa, *Polymer Materials Encyclopedia*, Vol. 2 Salamone, J. C. (ed.), CRC Press, New York, 1966, p. 941.
4. K. Fujiki, N. Tsubokawa and Y. Sone, *Polym. J.* **22**, 661 (1990).
5. N. Tsubokawa, K. Fujiki and Y. Sone, *Polym. J.* **20**, 213 (1988).
6. N. Tsubokawa, *J. Polym. Sci., Polym. Chem. Ed.* **21**, 705 (1983).
7. N. Tsubokawa, A. Yamada and Y. Sone, *Polym. Bull.* **10**, 62 (1983).
8. N. Tsubokawa, *Nippon Kagaku Kaishi* **9**, 1012 (1993).
9. M. Levy and M. Szwarc, *J. Chem. Phys.* **22**, 1621 (1954).
10. D. Hey and G. Williams, *Discuss. Faraday Soc.* **14**, 216 (1953).
11. K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda and N. Takashina, *Carbon* **13**, 443 (1975).
12. K. Ohkita, N. Tsubokawa and E. Saitoh, *Carbon* **16**, 41 (1978).
13. A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.* **24**, 405 (1986).
14. N. Tsubokawa and K. Yanadori, *Kobunshi Ronbunshu* **49**, 865 (1992).
15. N. Tsubokawa and S. Handa, *J. Jpn. Soc. Color Mater.* **66**, 468 (1993).
16. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer, *Macromolecules* **26**, 2987 (1993).
17. E. Yoshida, T. Ishizone, A. Hirao, S. Nakahama, T. Takata and T. Endo, *Macromolecules* **27**, 3119 (1994).
18. N. Tsubokawa, S. Yoshikawa, K. Maruyama, T. Ogasawara and K. Saitoh, *Polym. Bull.* **39**, 217 (1997).
19. K. Ohkita, M. Uchiyama and M. Shimomura, *Kobunshi Ronbunshu* **36**, 465 (1976).
20. G. Mino, S. Kaizerman and Rasumussen, *J. Polym. Sci.* **38**, 393 (1959).
21. G. Mino and S. Kaizerman, *J. Polym. Sci.* **31**, 242 (1958).
22. J. B. Donnet, G. Henrich and L. Geidreich, *Compt. Rend.* **249**, 97 (1959).
23. K. Ohkita, H. Kasahara, N. Ishizuke and Y. Itagaki, *Nippon Gomu Kyokaishi* **30**, 36 (1963).
24. J. W. C. Spachman, *Chem. Ind. (London)* 1532 (1961).
25. K. Ohkita and K. Fukushima, *Japan Plastics* **3**(3), 6 (1969).
26. K. Ohkita and K. Fukushima, *Japan Plastics* **3**(4), 25 (1969).