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GRAFTING OF BRANCHED POLYMERS ONTO CARBON BLACK SURFACE: RADICAL POSTPOLYMERIZATION INITIATED BY PENDANT AZO GROUPS OF GRAFTED POLYMER ON THE SURFACE

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ABSTRACT

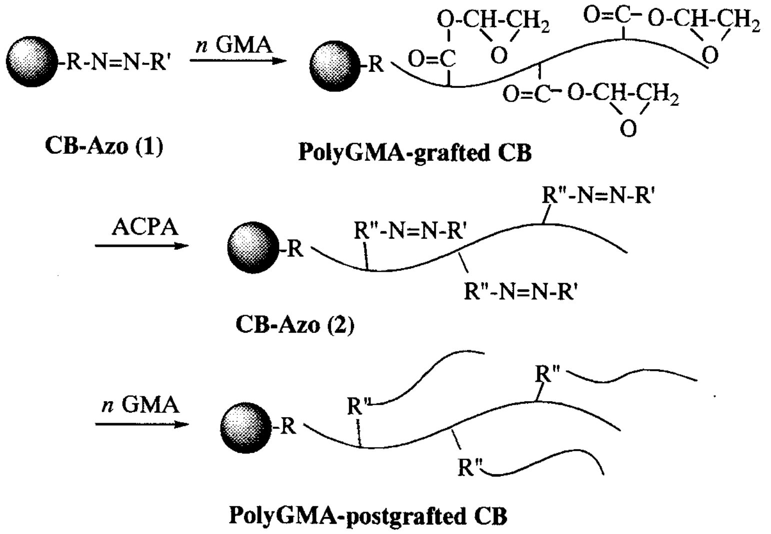
The grafting of highly branched polymer onto carbon black surface by postpolymerization of glycidyl methacrylate (GMA) initiated by pendant azo groups introduced to grafted polyGMA on the surface was investigated. The graft polymerization of GMA onto carbon black was achieved by use of azo groups introduced onto the surface: the percentage of grafting (the proportion of grafted polymer to carbon black) and surface density of grafted polymer to carbon black were determined to be 35.4% and 0.39 mg/m^2, respectively. The introduction of pendant azo groups to grafted polyGMA chain on carbon black was successfully achieved by the reaction of pendant glycidyl groups with 4,4'-azobis(4-cyanopentanoic acid) using (α-picolin as a catalyst: the amount of pendant azo groups was determined to be 0.23 mmol/g. It was found that the postpolymerization of GMA was initiated by the pendant azo groups of polyGMA-grafted carbon black and branched polymer was grafted onto carbon black surface: the total grafting of polyGMA was increased from 35.4% (0.39 mg/m^2) to 47.5% (0.52 mg/m^2) after the postpolymerization. By repeating the above procedure, i.e., introduction of pendant azo groups and and postpolymerization, highly branched polymers were grafted onto carbon black surface. Branched polymer-grafted carbon black gave a stable colloidal dispersion in good solvents for grafted polymer.

INTRODUCTION

Carbon black has excellent properties, such as heat, chemical and weather resistance, light weight, electroconductivity, and low thermal expansion [1, 2]. It is also used industrially as a deep black pigment for polymer materials. In general, dispersing of carbon black uniformly into a polymer matrix or an organic solvent is very difficult. In addition, mechanical properties of carbon black-polymer composites are known to depend not only on the mechanical properties of the polymer matrix, but also on the properties of interfacial regions between the carbon black surface and the matrix polymer. Therefore, surface modification of carbon black was achieved by the grafting of various polymers onto carbon black using radical, cationic, and anionic polymerization initiated by azo [3] and peroxyester [4], acylium perchlorate [5], and potassium carboxylate groups [6,7] introduced onto the surface, respectively.

Pendant functional groups of grafted polymer on inorganic particles are successfully used for the functionalization of the particle surface. For instance, Shimomura and his coworkers have reported the immobilization of enzyme, such as glucose oxidase, to grafted poly(acrylic acid) chains on magnetite and silica surfaces by the reaction of the pendant carboxyl groups with glucose oxidase in the presence of condensing agent [8,9]. In addition, the cross-linking reaction of surface poly(styrene-co-maleic anhydride) grafted onto colloidal silica surface with diol [10] and the radical graft polymerization of vinyl monomers to hydrophilic macromer adsorbed onto the colloidal silica surface have been reported by Yoshinaga et al. [11].

On the other hand, we converted pendant carboxyl groups of grafted polymer on carbon black into potassium carboxylate [12] and acylium perchlorate groups [13]. And then, to prepare polymer-grafted carbon black with higher percentage of grafting and to graft branched polymer onto the surface, the postpolymerization of vinyl monomers initiated by the pendant poatssium carboxylate and acylium perchlorate groups of grafted polymer on the surface was achieved.



Scheme 1

In the present paper, the introduction of azo groups by use of pendant functional groups of grafted polymer on carbon black surface and the radical postpolymerization of vinyl monomers initiated by the pendant azo groups of grafted polymer on carbon black surface was investigated (Scheme 1). The dispersibility of branched polymer-grafted carbon black was also discussed.

EXPERIMENTAL

Materials and Reagents

Carbon black used was channel black Neospectra II (Columbian Carbon Co.). Specific surface area, particle size, the amount of phenolic hydroxyl and carboxyl group, DBP absorption number, tinting strength, and pH were 906 m^2/g, 13 nm, 0.24 mmol/g and 0.40 mmol/g, 1.9 mL/g, 93, and 3.0, respectively. The carbon black was dried *in vacuo* at 110°C before use.

Glycidyl methacrylate (GMA) was dried over potassium carbonate and distilled under reduced pressure. Tolylene 2,4-diisocyanate (TDI) was distilled under reduced pressure just before use. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) was recrystallized from methanol and dried *in vacuo* at room temperature. Tetrahydrofuran (THF) was refluxed over sodium and distilled. α–Picoline, *n*-hexane, and chloroform were used without further purification.

Introduction of Azo Groups onto Carbon Black

Azo groups were introduced onto carbon black surface by the reaction of ACPA with isocyanate groups which were introduced onto the surface by the reaction of carboxyl and phenolic hydroxyl groups on the surface with TDI. The detailed procedures were described in the previous paper [3]. The treated carbon black was stored in the dark below 0°C. The treated carbon black having azo groups was abbreviated as CB-Azo (1).

Graft Polymerization of GMA

Into a glass ample, 0.30 g of carbon black and 10.0 mL of GMA were charged. The ampule was frozen in a liquid nitrogen bath, thawed three times, and sealed *in vacuo*. The sealed ampule was heated with shaking. After a definite time, the product was poured into a large excess of *n*-hexane. The precipitate was filtered and dried *in vacuo* at 60°C. The conversion was calculated by the following equation:

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

Introduction of Pendant Azo Groups to Grafted Polymer on Carbon Black

The introduction of pendant azo groups to grafted polyGMAchain on carbon black surface was achieved by the reaction of the pendant glycidyl groups with ACPA. A typical example is as follows. Into a 100 mL flask, 0.30 g of polyGMA-grafted carbon black, 10.0 mL of THF, 1.0 g of ACPA, and 0.1 g of (α-picoline as a catalyst were charged. The mixture was stirred for 24 hours with a magnetic stirrer at room temperature under dry nitrogen. After the reaction, the resulting mixture was repeatedly washed with THF and dried *in vacuo* at room temperature. The treated carbon black was immediately used for the following polymerization. The treated carbon black having pendant azo groups of grafted polymer on the surface was abbreviated as CB-Azo (2).

Postpolymerization of GMA Initiated by CB-Azo (2)

Into a glass ample, 0.30 g of CB-Azo (2) and 10.0 mL of GMA were charged. The postpolymerization and precipitation of product were carried out by the same method as mentioned above.

Percentage of Grafting, Postgrafting and Overall Grafting

To isolate the polymer-grafted carbon black and polymer-postgrafted carbon black from the reaction mixture containing ungrafted polymer, the product was dispersed in chloroform and the dispersion was centrifuged at 1.2×10^4 rpm until carbon black was precipitated completely. The carbon black precipitated was dispersed again in chloroform and the dispersion was centrifuged. The procedures were repeated until no more polymer was detected in the supernatant solution. Then, the resulting carbon black was dried *in vacuo* at 60°C. The percentage of grafting, overall grafting, and surface density of polymer were calculated by the following equations:

$$\text{Grafting(\%)} = \frac{\text{Polymer grafted (g)}}{\text{CB-Azo (1) used (g)}} \times 100$$

$$\text{Overall grafting (\%)} = \frac{\text{All of polymers grafted (g)}}{\text{Net weight of carbon black used (g)}} \times 100$$

$$\text{Surface density of polymer (mg/m}^2\text{)} = \frac{\text{Polymer (mg)}}{\text{Surface area of carbon black used (m}^2\text{)}}$$

Dispersibility of Branched Polymer-Grafted Carbon Black

Polymer-grafted carbon black (0.30 g) was dispersed in 100 mL of THF and allowed to stand at room temperature. After a definite time, 5.0 mL of dispersion liquid was taken out with a pipette and the content of the carbon black was determined. The stability of dispersion was estimated by the content of the carbon black in the dispersion. The dispersibility of polymer-grafted carbon black was estimated by the following equation:

$$\text{Dispersibility (\%)} = \frac{\text{Carbon black dispersed after standing (g)}}{\text{Carbon black dispersed before standing (g)}} \times 100$$

RESULTS AND DISCUSSION

Introduction of Azo Groups onto Carbon Black Surface

Channel black Neospectra II has reactive functional groups, such as carboxyl groups and phenolic hydroxyl groups and these functional groups were used as sites for the support of initiator [1]. We achieved the introduction of azo groups onto the carbon black surface by the following two steps: (1) introduction of

TABLE 1. Graft Polymerization of GMA Initiated by CB-Azo (1)

Carbon black	Conversion %	Grafting %	Surface Density mg/m^2
None	trace		
Untreated	trace	0	0
CB-Azo (1)	*5.2*	*35.4*	0.39

CB, 0.30 g; GMA, 10.0 mL; 70°C; 1 hour.

isocyanate groups onto the surface by the reaction of surface reactive functional groups with TDI and (2) introduction of azo groups onto the surface by the reaction of isocyanate groups introduced onto the surface with ACPA [1,3]. The contents of azo groups of carbon black (CB-Azo (1)) used in this study were determined to be 0.22 mmol/g by elemental analysis.

Graft Polymerization of GMA

The graft polymerization of GMA was carried out in the presence of CB-Azo (1) at 70°C under vacuum. The results are shown in Table 1. The polymerization of GMA scarcely proceeded in the absence of carbon black and in the presence of untreated carbon black. On the contrary, the polymerization of GMA was initiated in the presence of CB-Azo (1), and polyGMA-grafted carbon black having pendant glycidyl groups was obtained. This indicates that the polymerization of GMA is initiated by surface radical formed by the decomposition of surface azo groups introduced onto carbon black surface.

Figure 1 shows the effect of temperature on the graft polymerization of GMA initiated by CB-Azo (1). It was found that the conversion and percentage of grafting (surface density of grafted polymer) increased with increasing polymerization temperature: the percentage of grafting reached to 58% (0.64 mg/m^2) at 80°C. This suggests that the surface azo groups on carbon black are effectively decomposed at higher temperature.

The relationship between polymerization time and conversion (the percentage of grafting and surface density) was also investigated at 70°C. The results are shown in Figure 2. The conversion increased with progress of the polymerization, but the percentage of grafting became constant about 35% (0.39 mg/m2) after 1 hour. This result suggests that azo groups on the surface were blocked by grafted polymer chains with progress of the polymerization.

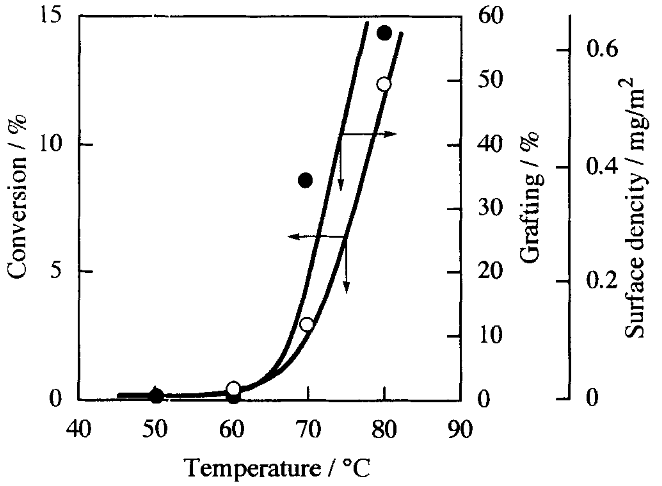


Figure 1. Effect of temperature on the graft polymerization of GMA initiated by CB-Azo (1). CB-Azo (1), 0.30 g; GMA, 10.0 mL; 1 hour.

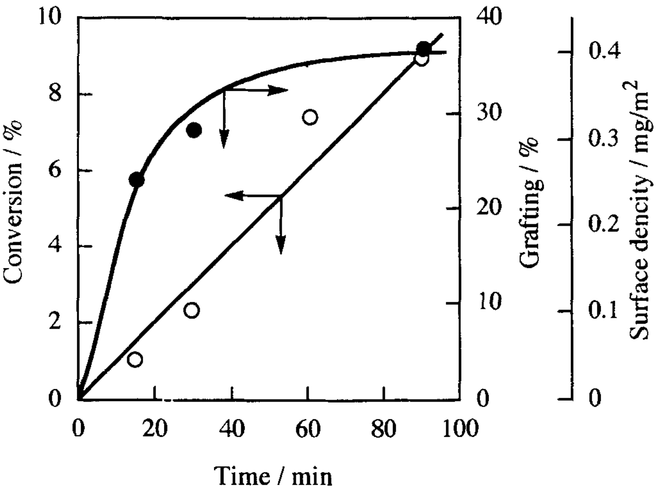


Figure 2. Graft polymerization of GMA onto carbon black initiated by CB-Azo (1) CB-Azo (1), 0.30 g; GMA, 10.0 mL; 70°C.

Introduction of Azo Groups to Grafted PolyGMA on Carbon Black

Since grafted polyGMA on carbon black has reactive pendant glycidyl groups, it is expected that these groups are used for the support of radical initiator. Therefore, the introduction of azo groups to the grafted polymer chains of polyGMA-grafted carbon black by the reaction of pendant glycidyl groups with

TABLE 2. Postpolymerization of GMA Initiated by CB-Azo (2)

Carbon black	Conversion %	Overall grafting %	Surface density mg/m^2
PolyGMA-grafted CB	0.1	35.4	0.39
CB-Azo(2)	5.2	47.5	0.52

CB-Azo (2), 0.30 g; GMA, 10.0 mL; 70°C; 1 hour.

ACPA was investigated: polyGMA-grafted carbon black, whose percentage of grafting was 35.4% (0.39 mg/m^2), was treated with ACPA in the presence of α-picoline as a catalyst at room temperature.

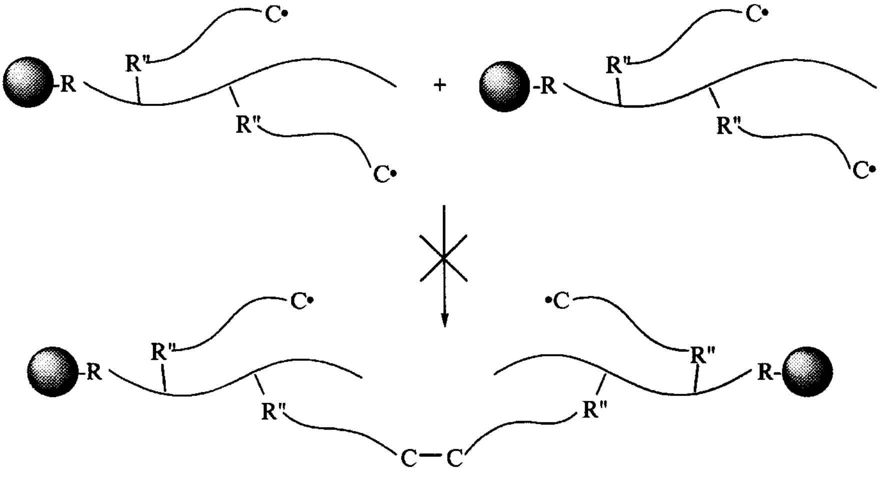
The contents of azo groups introduced onto polyGMA-grafted carbon black were determined to be 0.23 mmol/g by elemental analysis. This indicates that 9.2% of pendant glycidyl groups of grafted polyGMA on carbon black were reacted with ACPA. The carbon black having pendant azo groups in grafted polyGMA chain was abbreviated as CB-Azo (2).

Postpolymerization of GMA

The postpolymerization of GMA was carried out in the presence of CB-Azo (2) at 70°C. The results are shown in Table 2. The polymerization of GMA was barely initiated in the presence of polyGMA-grafted carbon black having no azo groups. On the contrary, the polymerization of GMA was successfully initiated in the presence of CB-Azo (2). This indicates that the postpolymerization of GMA is initiated by pendant radicals formed by the decomposition of pendant azo groups of grafted polyGMA chain on carbon black and branched polymer-grafted carbon black is proceeded.

The postgrafted polymer chains on carbon black were barely isolated from the surface. Therefore, the molecular weight of the ungrafted polymer formed during the postpolymerization of GMA initiated by CB-Azo (2), instead of postgrafted polymer chain, was measured by GPC. As a result, the molecular weight and the molecular weight distribution of the ungrafted polymer were determined to be $5.3\text{x}10^{5}$ and 1.41, respectively.

During the postpolymerization, the formation of gel was not observed at all. This suggests that the coupling reaction between the growing polymer radicals from the carbon black surface barely proceeds, because the growing polymer radicals from the surface are fixed on solid surface (Scheme 2).



Scheme 2

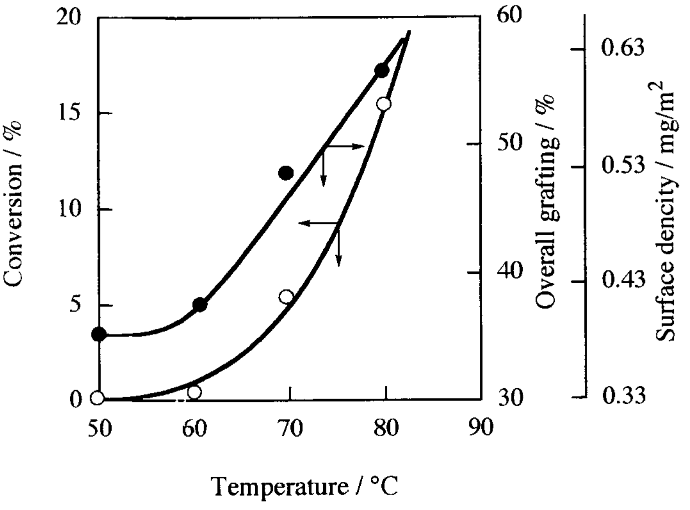


Figure 3. Effect of temperature on the postpolymerization of GMA initiated by CB-Azo (2). CB-Azo (2), 0.30 g; GMA, 10.0 mL; 1 hour.

Figure 3 shows the effect of temperature on the postpolymerization of GMA in the presence of CB-Azo (2). It was found that the conversion increased with increasing polymerization temperature. The percentage of overall grafting also increased and reached to 56% (0.62 mg/m^2) at 80°C.

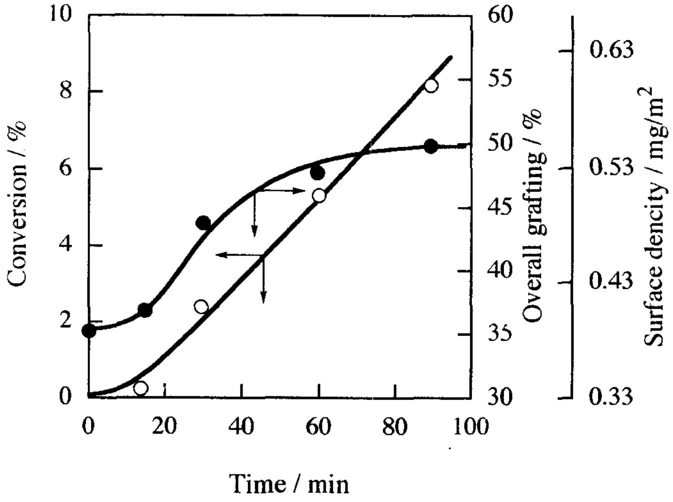


Figure 4. Postpolymerization of GMA initiated by CB-Azo (2). CB-Azo (2),0.30 g; GMA, 10.0 mL; 70°C.

The relationship between polymerization time and conversion (the percentage of overall grafting and surface density) was shown in Figure 4. The conversion increased with progress of the polymerization, but the percentage of overall grafting became constant about 50% (0.55 mg/m^2) after 1 hour. The result suggests that the postpolymerization of GMA is initiated by pendant azo groups of polymer-grafted carbon black, but chain transfer reaction of propagating radical proceeded at last stage of the postpolymerization. In addition, the propagation from grafted chains is considered to be inhibited by the grafted polymer chains on the surface.

Effect of the Concentration of CB-Azo (2) on the Postpolymerization Rate

It is well known that in the radical polymerization, the polymerization rate has a 0.5 order dependence on the initiator concentration because of bimolecular termination of growing polymer radicals.

The effect of concentration of CB-Azo (2) ([CB-Azo(2)]) on the postpolymerization rate (Rp) was investigated. The result is shown in Figure 5. It was found that the postpolymerization rate has 0.85 order dependence on the CB-Azo (2) concentration. The value is larger than that of a ordinally radical polymerization system. The same tendency was observed in radical graft polym-

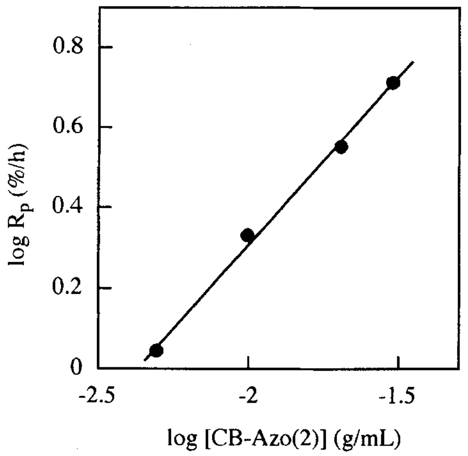


Figure 5. Relationship between postpolymerization rate (Rp) and CB-Azo (2) concentration ([CB-Azo (2)]). Polymerization conditions are given in Figure 4.

erization initiated by the system consisting of ceric ion and alcoholic hydroxyl groups on a powder surface [14]. These results suggest that unimolecular termination of growing polymer radicals from the grafted polymer chains of polymer-grafted carbon black proceeded in the initial stage of the polymerization.

This may be due to the fact that the bimolecular termination of polymer radicals is inhibited because the growing polymer radical on the surface are fixed on the solid (carbon black) surface.

Repeating Postpolymerization of GMA

The introduction of azo groups to pendant glycidyl groups of branched polymer-grafted carbon black was repeated and repeating postpolymerization was investigated. Branched polyGMA grafted carbon black having pendant azo groups in the grafted branched polyGMA, i.e., CB-Azo (3), was also prepared by the reaction of ACPA with pendant glycidyl groups of branched polyGMA-grafted carbon black obtained from the postpolymerization using CB-Azo (2), as the same method of preparation of CB-Azo (2). The contents of azo groups introduced onto polymer-grafted carbon black (CB-Azo (3)) were determined to be 0.27 mmol/g by elemental analysis.

The repeating postpolymerization of GMA was found to be initiated by CB-Azo (3) to give highly branched polymer-grafted carbon black. The relationship

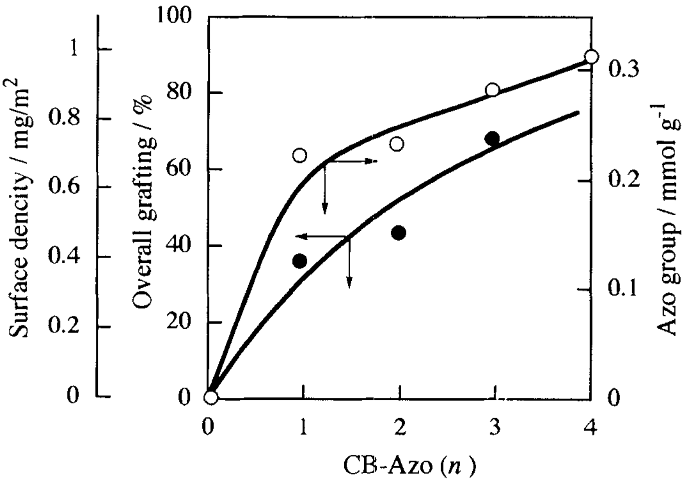


Figure 6. Repeating postpolymerization of GMA initiated by azo groups introduced onto branched polymer-grafted carbon black (CB-Azo (*n*). CB-Azo (*n*), 0.30 g; GMA, 10.0 mL; 70°C; 30 min.

between the CB-Azo (n) and overall grafting or amount of azo groups introduced to grafted polyGMA on carbon black was shown in Figure 6. In Figure 6, CB-Azo (0) indicates untreated carbon black. The percentage of overall grafting indicates the values after the repeating postpolymerization of GMA in the presence of CB-Azo (*n*).

The percentage of overall grafting and the amount of azo groups increased with increasing repeating times of introduction of azo groups to grafted polyGMA on carbon black and the postpolymerization of GMA. These results suggest that the polymerization of GMA is initiated in the presence of polyGMA-grafted carbon black having pendant azo groups and highly branched polymers are grafted on the surface. However, the increase of overall grafting became small with increasing repeating times. This may be due to the fact that pendant azo groups of branched polyGMA on the surface were blocked by grafted polymer chains with increasing repeating times of the postpolymerization.

Dispersibility of PolyGMA-Grafted Carbon Black

The stability of carbon black dispersion in THF before and after postpolymerization was compared with that of untreated carbon black. The results are shown in Figure 7. Untreated carbon black precipitated completely after 1 day. The precipitation of polyGMA-grafted carbon black was considerably delayed even

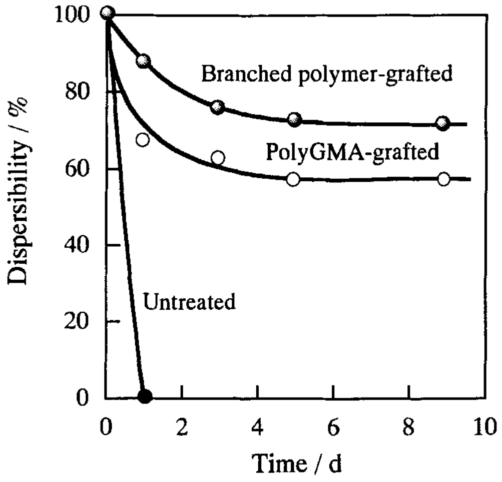


Figure 7. Dispersibility of polyGMA-grafted (grafting = 35.4%; surface density = 0.39mg/m^2) and branched polymer-grafted carbon black (overall grafting = 49.8%; surface density = 0.55 mg/m^2) in THF.

before postpolymerization, but after the postpolymerization branched polymer-grafted carbon black gave the most stable dispersion in THF. This suggests that grafted branched polymer chains on carbon black surface effectively interfere with the aggregation of carbon black particles in the good solvent of grafted polymer.

CONCLUSIONS

- The polymerization of GMA was initiated by azo groups introduced onto carbon black surface and polymer having pendant glycidyl groups was grafted onto the surface.
- The introduction of pendant azo groups to grafted polyGMA on carbon black was successfully achieved by the reaction of the pendant glycidyl groups with ACPA.
- The postpolymerization of GMA was initiated by pendant azo groups of grafted polyGMA on carbon black to give branched polymer-grafted carbon black. By repeating the above procedure, highly branched polymers were grafted onto carbon black surface.
- Branched polymer-grafted carbon black gave a stable colloidal dispersion in a good solvent for the grafted polymer.

REFERENCES

[1] N. Tsubokawa, *Prog. Polym. Sci.*, 17, 417 (1992).

[2] N.Tsubokawa, *Kobunshi*, 45, 412 (1996).

[3] K. Fujiki and N. Tsubokawa, Y. Sone, *Polym. J.*, 2 2, 661 (1990).

[4] N. Tsubokawa, K. Fujiki, and Y. Sone, *Polym. J.*, 20, 213 (1988).

[5] N. Tsubokawa, *J. Polym. Sic. Polym. Chem. Ed.*, *21*, 705 (1983).

[6] N. Tsubokawa, A. Funaki, Y. Hada, and Y. Sone, *J. Polym. Sic. Polym. Chem. Ed.*, *20*, 3297 (1982).

[7] N. Tsubokawa, Y. Yamada, and Y. Sone, *Polym. Bull.*, *10*, 62 (1983).

[8] M. Shimomura, H. Kikuchi, H. Matsumoto, T. Yamauchi, and S. Miyauchi, *Polym. J.*, *2 7*, 974 (1995).

[9] N. Sugiyama, T. Yamauchi, M. Shimomura, and S. Miyauchi, *Polym. Preprints, Japan*, *45*, 567 (1996).

[10] K.Yoshinaga, and K. Nakanishi, *Composite Interfaces*, 2, 71 (1994).

[11] K.Yoshinaga, T.Yokoyama, and T. Kito, *Polym. Adv. Technol.*, *4*, 38 1993).

[12] N. Tsubokawa,K. Fujiki, and T. Sasaki, *Kobunshi Ronbunshu*, *50*, 235 (1993).

[13] K. Fujiki, N. Motoji, H. Tsuchida, and N. Tsubokawa, *Polym. J.*, *26*, 571 (1994).

[14] N. Tsubokawa, and K. Seno, *J. Macromol. Sci., Pure Appl. Chem.*, *A31*, 1135 (1994).

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