

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Radical Graft Polymerization of Vinyl Monomers Initiated by A20 Groups Introduced Onto a Carbon Black Surface: Effect of azo Groups on Graft Polymerization

Kazuhiro Fujiki^a; Norio Tsubokawa^b; Yasuo Sone^b

^a Graduate School of Science and Technology Niigata University, Niigata, Japan ^b Department of Material and Chemical Engineering Faculty of Engineering, Niigata University, Niigata, Japan

To cite this Article Fujiki, Kazuhiro , Tsubokawa, Norio and Sone, Yasuo(1991) 'Radical Graft Polymerization of Vinyl Monomers Initiated by A20 Groups Introduced Onto a Carbon Black Surface: Effect of azo Groups on Graft Polymerization', *Journal of Macromolecular Science, Part A*, 28: 8, 715 – 731

To link to this Article: DOI: 10.1080/00222339108054052

URL: <http://dx.doi.org/10.1080/00222339108054052>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

RADICAL GRAFT POLYMERIZATION OF VINYL MONOMERS INITIATED BY AZO GROUPS INTRODUCED ONTO A CARBON BLACK SURFACE: EFFECT OF AZO GROUPS ON GRAFT POLYMERIZATION

KAZUHIRO FUJIKI

Graduate School of Science and Technology
Niigata University
8050, Ikarashi 2-nocho, Niigata 950-21, Japan

NORIO TSUBOKAWA* and YASUO SONE

Department of Material and Chemical Engineering
Faculty of Engineering
Niigata University
8050, Ikarashi 2-nocho, Niigata 950-21, Japan

ABSTRACT

The radical graft polymerization of vinyl monomers from carbon black initiated by azo groups introduced onto the surface was investigated. The introduction of azo groups onto carbon black surface was achieved by three methods: the reaction of 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (AIP) with (1) epoxide groups, which were introduced by the reaction of carbon black with chloromethyloxirane; (2) acyl chloride groups, which were introduced by the reaction of carboxyl groups on the surface with thionyl chloride; and (3) 3-chloroformyl-1-cyano-1-methylpropyl groups, which were introduced by the reaction of carbon black with 4,4'-azobis(4-cyanovaleric acid) and then thionyl chloride. The amount

of azo groups introduced onto the surface by the above methods was determined to be 0.07–0.19 mmol/g. The graft polymerization of methyl methacrylate was found to be initiated by azo groups introduced onto the carbon black surface. During the polymerization, poly(methyl methacrylate) was effectively grafted onto carbon black through propagation of the polymer from the radical produced on the surface by the decomposition of the azo groups. The percentage of grafting using carbon black having azo groups introduced by method 1 increased to 40%. It was also found that the graft polymerization of several vinyl monomers such as styrene, acrylonitrile, and acrylic acid was initiated by the azo groups introduced onto the surface and the corresponding polymer was effectively grafted onto the surface. Furthermore, the effect of the amount of carbon black having azo groups on the graft polymerization was investigated.

INTRODUCTION

The grafting of various polymers onto carbon black has been widely investigated [1]. For instance, polymer-grafted carbon black can be easily obtained when the polymerization of vinyl monomers is initiated by radical [2], anionic [3], and cationic [4] initiators in the presence of carbon black. The percentage of grafting of polymers and grafting efficiency, however, are less than 10% because the carbon black surface reacts with initiators in preference to growing polymer chains.

Therefore, it is necessary to initiate the polymerization from active sites introduced onto the surface of the carbon black to obtain polymer-grafted carbon black with a higher percentage of grafting [5, 6]. From this point of view, we reported the grafting of various polymers onto carbon black by anionic grafting from alkali metal carboxylate groups on carbon black [7, 8] and by cationic grafting from acylium perchlorate groups on carbon black [9, 10]. The radical grafting from carbon black, however, has been scarcely investigated.

In an earlier paper, we reported the radical graft polymerization of vinyl monomers from carbon black initiated by a redox system consisting of ceric ions and alcoholic hydroxyl groups introduced onto the surface [11] and the radical graft polymerization of vinyl monomers initiated by peroxyester groups introduced onto the surface [12]. Recently, we succeeded in radical grafting initiated by azo groups introduced onto the

TABLE 1. Properties of Carbon Blacks Used

Carbon black	BET surface area, m ² /g	pH	COOH, mmol/g	OH, mmol/g	C=O, mmol/g
Neospectra II ^a	906	3.0	0.40	0.24	0.92
Philblack O ^b	79.6	8.7	0	0.02	0.18

^aChannel black.

^bFurnace black.

ical Co., and 2,2'-azobis[2-(2-imidazolin-2-yl) propane] (AIP), obtained from Wako Pure Chemical Co., were dried *in vacuo* at room temperature before use.

Chloromethyloxirane was distilled twice under reduced pressure. Dioxane and benzene were refluxed over sodium and distilled twice. Pyridine was dried over potassium hydroxide with stirring for 24 h and then distilled. Other solvents and reagents were used without further purification.

Preparation of Carbon Black Having Epoxide Groups (Carbon Black 1)

The introduction of epoxide groups onto carbon black was achieved by the reaction of carboxyl and phenolic hydroxyl groups on the carbon black surface with chloromethyloxirane in the presence of NaOH according to a previous paper [17].

Preparation of Carbon Black Having Acyl Chloride Groups (Carbon Black 2)

Carbon black having acyl chloride groups was prepared by the reaction of carboxyl groups on the surface with thionyl chloride. The procedures were described in a previous paper [18].

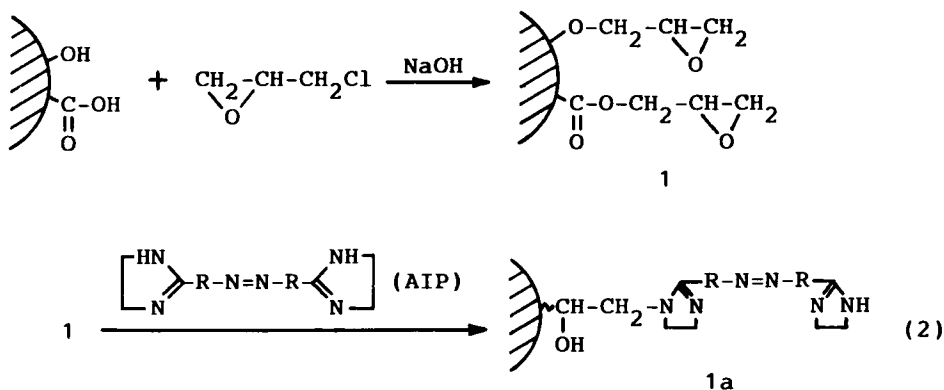
Preparation of Carbon Black Having 3-Chloroformyl-1-cyano-1-methylpropyl Groups (Carbon Black 3)

The introduction of carboxyl groups onto carbon black was achieved by the reaction of aromatic rings of the carbon black with 3-carboxy-1-cyano-1-methylpropyl radicals which formed by the thermal decomposition of ACV. Then the carbon black was treated with thionyl chloride to prepare carbon black 3. The procedures for the treatment were also described in previous papers [12, 18, 19].

Introduction of Azo Groups onto Carbon Black

The introduction of azo groups onto the carbon black surface was achieved by the following methods.

(1) *Preparation of Carbon Black 1a.* Carbon black 1a was prepared by the reaction of epoxide groups on the surface (carbon black 1) with AIP (Eq. 2).



Into a 200-mL flask, 5.0 g carbon black having epoxide groups, 1.0 g AIP, 50 mL dioxane, and 0.70 mL pyridine were charged. Then the reaction mixture was stirred with a magnetic stirrer for 8 h at 25°C under dry nitrogen. After the reaction, the resulting carbon black was repeatedly washed with methanol and dried *in vacuo* at room temperature. The treated carbon black was stored in the dark below 0°C.

(2) *Preparation of Carbon Black 2a.* Carbon black 2a was prepared by the reaction of acyl chloride groups on the surface (carbon black 2) with AIP (Eq. 3).

was heated at 70°C with shaking. After a definite time, the contents of the tube were poured into a large excess of a precipitant for the polymer. The precipitate was filtered and dried *in vacuo* at 40°C. The precipitant for poly(methyl methacrylate) (PMMA), polystyrene, and polyacrylonitrile was methanol. A large amount of water was used to precipitate poly(vinyl acetate).

When acrylic acid was used as the monomer, polymerization was stopped by adding hydroquinone and then unreacted monomer was removed by distillation under reduced pressure. The residue was dried *in vacuo* at 40°C.

The conversion was calculated according to

$$\text{conversion (\%)} = \frac{\text{precipitate obtained (g)} - \text{carbon black (g)}}{\text{monomer used (g)}} \times 100$$

Determination of Percentage of Grafting and Grafting Efficiency

The reaction product was dispersed in a solvent for the polymer with stirring, and the dispersion was centrifuged at 1.0×10^4 rpm until the carbon black was precipitated completely in order to isolate polymer-grafted carbon black from the product containing ungrafted polymer. The carbon black precipitated was extracted with a solvent for the polymer by using a Soxhlet apparatus until no more polymer was eluted in the reflux solvent. After extraction, the carbon black was dried *in vacuo* at 90°C. The dispersing and extracting solvents for polystyrene, PMMA, polyacrylonitrile, and poly(vinyl acetate) and poly(acrylic acid) were benzene, chloroform, *N,N*-dimethylformamide, and methanol, respectively.

The percentage of grafting and grafting efficiency were determined by the following equations:

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

$$\text{grafting efficiency (\%)} = \frac{\text{polymer grafted (g)}}{\text{total polymer formed (g)}} \times 100$$

The amount of polymer grafted was determined from the increment in weight of carbon black after graft polymerization.

RESULTS AND DISCUSSION

Introduction of Azo Groups onto Carbon Black

In a previous paper, the introduction of azo groups onto the carbon black surface was achieved by three methods [13]: (1) the reaction of 2,2'-azobis(2-cyano-*n*-propanol) (ACP) with acyl chloride groups on the surface, which were introduced by the reaction of carboxyl groups on the surface with thionyl chloride; (2) the reaction of ACV with isocyanate groups on the surface, which were introduced by treatment of carbon black with tolylene 2,4-diisocyanate; and (3) the reaction of 4,4'-azobis(4-cyanovaleryl chloride) (ACV-COCl) with hydroxyl groups on the surface.

In this research, azo groups were introduced onto the carbon black surface by the following three methods by using AIP.

(1) Carbon black **1a** was prepared by the reaction of AIP with epoxide groups, which were introduced by the reaction of carbon black with chloromethyloxirane (Eq. 2).

(2) Carbon black **2a** was prepared by the reaction of AIP with acyl chloride groups, which were introduced by the reaction of carboxyl groups on the surface with thionyl chloride (Eq. 3).

(3) Carbon black **3a** was prepared by the reaction of AIP with 3-chloroformyl-1-cyano-1-methylpropyl groups, which were introduced by the reaction of 3-carboxy-1-methylpropyl groups with thionyl chloride (Eq. 4). 3-Carboxy-1-cyano-1-methylpropyl groups were introduced by the reaction of carbon black with ACV [12, 19].

The amount of azo groups introduced onto the surface was determined by elemental analysis of nitrogen. The results are summarized in Table 2. As shown in Table 2, azo groups can be introduced onto the carbon black surface by the reactions shown in Eqs. (2), (3), and (4).

Confirmation of Initiating by Azo Groups Introduced onto Carbon Black

The graft polymerization of MMA was carried out in the presence of carbon black **1a** at 70°C, and the initiating ability of the azo groups on the surface was examined. Table 3 shows the results of the graft polymerization of MMA under several conditions.

TABLE 2. The Amount of Azo Groups Introduced onto a Carbon Black Surface

Carbon black	Introduction reaction	No.	N, %	Azo group, ^a mmol/g
Untreated Neospectra II	—	—	Trace	0
Untreated Philblack O	—	—	Trace	0
Neospectra II	Eq. (2)	1a	1.61	0.19
Neospectra II	Eq. (3)	2a	0.93	0.11
Philblack O	Eq. (4)	3a	0.69	0.07

^aDetermined by elemental analysis of nitrogen.

As shown in Table 3, although the thermal polymerization of MMA proceeded slightly even in the absence of initiator, the rate of polymerization was very low (No. 1). In the presence of untreated carbon black (Nos. 2 and 3), however, no polymerization of MMA was observed. This phenomenon suggests that in the presence of untreated carbon black, thermal polymerization is completely inhibited by such oxygen-containing groups on the carbon black as phenolic hydroxyl and quino-

TABLE 3. Graft Polymerization of MMA under Several Conditions^a

No.	Carbon black	Conversion, %	Grafting, %
1	None	0.7	—
2	Untreated Neospectra II	0	—
3	Untreated Philblack O	0	—
4	Neospectra II ~ $\text{CH}-\text{CH}_2$ (1) $\quad \quad \quad \diagdown \quad \diagup$ $\quad \quad \quad \text{O}$	0.2	0
5	Philblack O ~ COCl (3)	0	—
6	AIP-adsorbed Neospectra II	0.4	0
7	Neospectra II ~ R-N=N-R' (1a)	4.0	40.3
8	Philblack O ~ R-N=N-R' (3a)	3.9	38.5

^aCarbon black, 0.30 g; MMA, 10 mL; 70°C; 6 h.

nic oxygen groups. Furthermore, the graft polymerization of MMA in the presence of Neospectra II having epoxide groups (carbon black 1) was examined (No. 4); carbon black 1 was found to have no ability to initiate polymerization. In the presence of Philblack O having chloroformyl groups (carbon black 3) (No. 5), no polymerization of MMA was observed.

On the contrary, the polymerization of MMA was found to be initiated both in the presence of carbon black 1a and in the presence of 3a, and PMMA was grafted onto the surface (Nos. 7 and 8).

To investigate initiation by azo groups on the surface, the initiating activity of AIP-adsorbed carbon black was evaluated (No. 6). AIP-adsorbed carbon black was prepared by the treatment of untreated Neospectra II with AIP in a manner similar to the introduction of azo groups. As shown in Table 3, AIP-adsorbed carbon black had no ability to initiate polymerization. This suggests that AIP adsorbed on the carbon black surface during treatment for the introduction of azo groups is completely removed by washing with methanol after the treatment.

Based on the above results, it is concluded that the polymerization of MMA is initiated by azo groups introduced onto the surface of the carbon black.

Graft Polymerization of MMA Initiated by Azo Groups on the Carbon Black

The graft polymerization of MMA initiated by azo groups introduced onto the carbon black surface was investigated. Figure 1 shows the time-conversion curve and the time-percentage of grafting curve for the graft polymerization of MMA initiated by carbon black 1a. It is apparent that PMMA is grafted onto the surface and that the percentage of grafting reaches about 40% after 6 h. The grafting efficiency was 30–50% in this graft polymerization. These values are almost equal to those obtained from polymerization initiated by azo groups introduced by the reaction of ACP with acyl chloride groups on carbon black according to the method described in a previous paper [13].

To evaluate the adsorption of PMMA onto the surface, untreated Neospectra II was mixed with ungrafted PMMA. The amount of the PMMA remaining on the surface after extraction with chloroform was negligibly small. This indicates that it is not necessary to take into account the effect on grafting of the adsorption of ungrafted PMMA produced during polymerization.

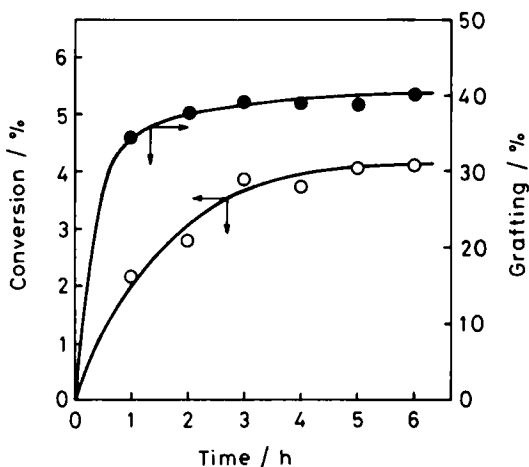


FIG. 1. Graft polymerization of MMA initiated by carbon black **1a**. Carbon black, 0.30 g; MMA, 10 mL; 70°C.

Figure 2 shows the results of the graft polymerization of MMA initiated by carbon black **2a** as an initiator. The conversion and the percentage of grafting after 6 h reached 3.8 and 37%, respectively. From these results, carbon black **2a** is found to have the ability to initiate the graft polymerization of MMA. The initiating activity of carbon black **2a** and the percentage of grafting, however, were slightly lower than those of carbon black **1a**. This may be due to the lower azo group content of carbon black **2a** than of carbon black **1a**. The grafting efficiency was determined to be 33–51%. In addition, these values were practically equal to those obtained from the polymerization using azo groups introduced by the reaction of ACV-COCl with hydroxyl groups on the carbon black surface.

As previously reported, the amounts of azo groups introduced by the reaction of ACV with acyl chloride groups on the surface and by the reaction of ACV-COCl with hydroxyl groups on the surface were 0.18 and 0.13 mmol/g, respectively [13]; each value is found to be almost equal to azo group contents of carbon black **1a** and **2a**, as shown in Table 2. These results suggest that the initiating activity of azo groups introduced onto the surface is influenced by the content rather than by the bonding structure.

The graft polymerization of MMA using carbon black **3a** as an initia-

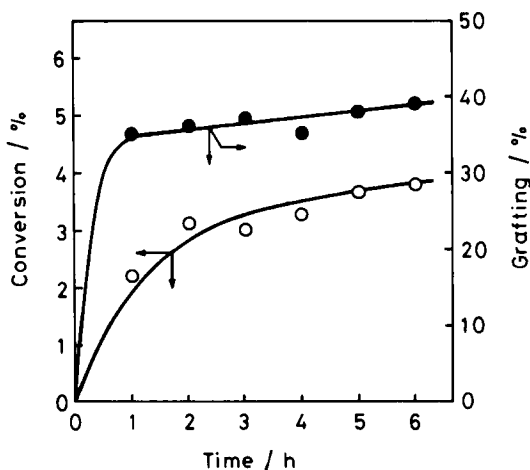


FIG. 2. Graft polymerization of MMA initiated by carbon black **2a**. Polymerization conditions are given in Fig. 1.

tor was examined. Figure 3 shows the time-conversion and time-percent-age curves of grafting. The conversion and the percentage of grafting increased gradually as the polymerization proceeded. These values reached 3.8 and 38%, respectively, after 6 h. The grafting efficiency was determined to be 32–47% during the graft polymerization of MMA. From the results, it is apparent that carbon black **3a** (furnace black Philblack O with azo groups on the surface) has an initiating activity for graft polymerization.

The azo groups on the surface are considered to produce both surface radicals and 1-(2-imidazoline-2-yl)-1-methylethyl radicals by their decomposition (Eq. 1). The former initiates graft polymerization, but the latter produces ungrafted polymer. Based on the grafting efficiency values, ungrafted polymer is produced mainly by 1-(2-imidazoline-2-yl)-1-methylethyl radicals rather than by a chain transfer reaction of growing polymer radicals from the surface.

Effect of the Amount of Carbon Black on the Graft Polymerization

The effect of the amount of carbon black **1a** used as an initiator on the graft polymerization of MMA was examined. The results are shown in Fig. 4. The conversion increases with an increase in the amount of

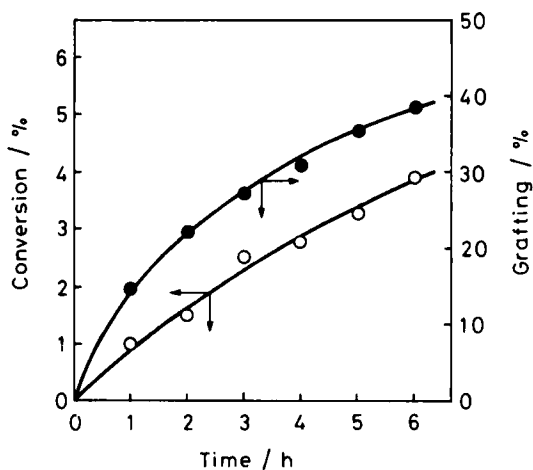


FIG. 3. Graft polymerization of MMA initiated by carbon black 3a. Polymerization conditions are given in Fig. 1.

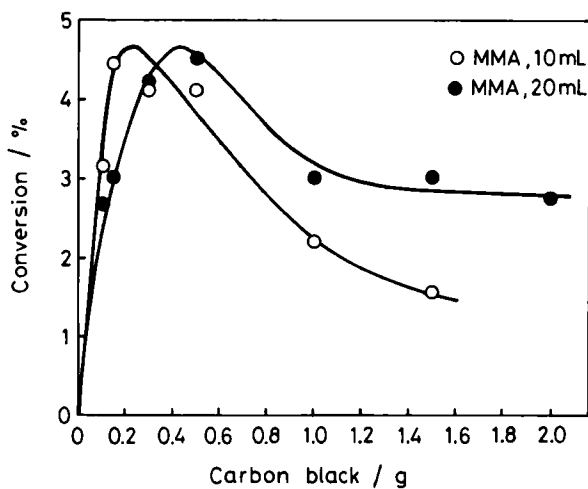


FIG. 4. Effect of the amount of carbon black 1a on the graft polymerization of MMA. 70°C; 6 h.

carbon black and reaches a maximum value. Then the conversion decreases gradually as the amount of carbon black increases. As is evident from the results, there exists an optimum amount of carbon black having azo groups as an initiator. The optimum was in the range of about 0.15–0.30 g when 10 mL of MMA was used, and about 0.30–0.50 g when 20 mL of MMA was used. The optimum amount of carbon black in 20 mL of MMA shifted to twice as much as that in 10 mL of MMA as the amount of MMA used was doubled.

Figures 5 and 6 show the time-conversion and the time-percentage of grafting curves when using 0.15 and 0.30 g of carbon black **1a** as the initiator, respectively. The conversion and the percentage of grafting using 0.15 g of carbon black **1a** are somewhat larger than those using 0.30 g of carbon black **1a**. The grafting efficiencies in each case, however, were almost equal (37–50 and 30–50%).

Based on these results, it seems that the decrease of conversion below the optimum amount of carbon black is due to the small azo group content on the carbon black surface. On the other hand, above the optimum amount of carbon black, the decrease of conversion seems to be due to considerable heterogeneous polymerization; that is, azo groups on the carbon black surface will not act effectively as an initiator because of insufficient diffusion of carbon black into the monomer solution.

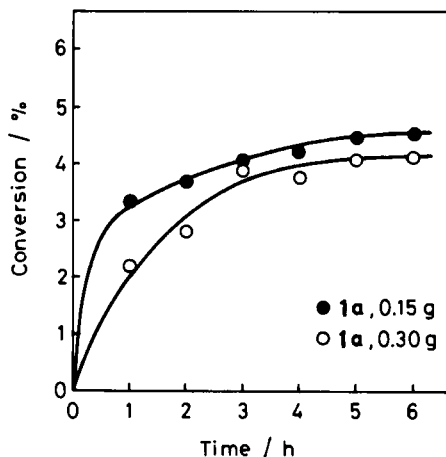


FIG. 5. Graft polymerization of MMA initiated by carbon black **1a**. MMA, 10 mL; 70°C.

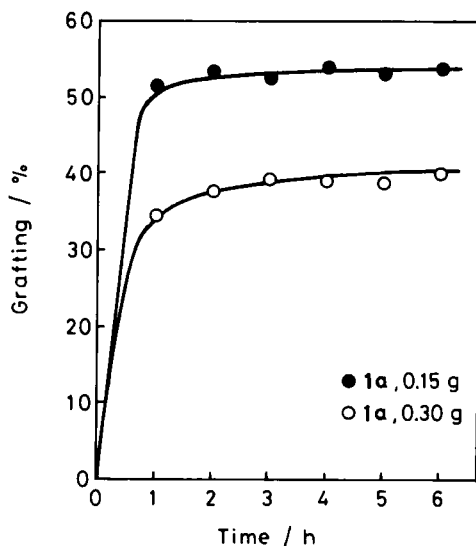


FIG. 6. Relationship between polymerization time and percentage of grafting using carbon black **1a** as an initiator.

Graft Polymerization of Several Vinyl Monomers

By using carbon black **1a** as an initiator, graft polymerizations of styrene, vinyl acetate, acrylonitrile, and acrylic acid were carried out. The polymerizability of these monomers was compared with MMA, and the results are summarized in Table 4. In a previous paper we reported

TABLE 4. Graft Polymerization of Several Vinyl Monomers Initiated by Carbon Black **1a**^a

Monomer	Time, h	Conversion, %	Grafting, %
Styrene	8	1.8	29.8
Vinyl acetate	8	2.0	25.1
Methyl methacrylate	6	4.1	40.3
Acrylic acid	2	12.3	78.5
Acrylonitrile	2	18.8	73.1

^aCarbon black, 0.30 g; monomer, 10 mL; 70°C.

that peroxyester groups introduced onto the carbon black surface had the ability to initiate the polymerization of vinyl monomers with positive e -values, such as MMA and acrylic acid, but no ability to initiate those with negative e -values, such as styrene and vinyl acetate [12, 20]. On the contrary, azo groups introduced onto the surface had the ability to initiate the polymerization of various vinyl monomers regardless of their e -values, although the polymerization of vinyl monomers with negative e -values was more retarded than those with positive e -values [13, 20].

As is evident from Table 4, the graft polymerization of styrene, vinyl acetate, acrylonitrile, and acrylic acid is also initiated by azo groups introduced onto the surface of carbon black, and the corresponding polymer is effectively grafted onto the surface although the polymerization of styrene and vinyl acetate with negative e -values is more retarded than that of the others with their positive e -values. The carbon black obtained from these polymerizations produced a stable colloidal dispersion in a good solvent for the grafted polymer. The precipitation of carbon black particles from the dispersion of carbon black obtained from the graft polymerization was barely observed after 30 days. Therefore, carbon black with azo groups is useful for a higher percentage of grafting of various vinyl polymers onto a surface.

REFERENCES

- [1] J. B. Donnet, *Carbon*, **20**, 266 (1982).
- [2] K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and N. Takashina, *Ibid.*, **13**, 443 (1975).
- [3] K. Ohkita, N. Nakayama, and T. Tsujita, *Ibid.*, **16**, 155 (1978).
- [4] K. Ohkita, N. Nakayama, and M. Shimoura, *Ibid.*, **18**, 277 (1980).
- [5] N. Tsubokawa, *Nippon Gomu Kyokaishi*, **58**, 306 (1985).
- [6] N. Tsubokawa and T. Endo, *Kinou Zairyoh*, **8**, 13 (1988); *Tanso*, No. 140, 322 (1989).
- [7] N. Tsubokawa, A. Funaki, Y. Hada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3297 (1982).
- [8] N. Tsubokawa, T. Ohyama, A. Yamada, and Y. Sone, *Ibid.*, **23**, 489 (1985).
- [9] N. Tsubokawa, Yu Jian, and Y. Sone, *Ibid.*, **26**, 2715 (1988).
- [10] N. Tsubokawa, *Ibid.*, **22**, 1515 (1984); **25**, 1979 (1987).
- [11] N. Tsubokawa, K. Fujiki, and Y. Sone, *J. Macromol. Sci. - Chem.*, **A25**, 1159 (1988).

- [12] N. Tsubokawa, K. Fujiki, and Y. Sone, *Polym. J.*, **20**, 213 (1988).
- [13] K. Fujiki, N. Tsubokawa, and Y. Sone, *Ibid.*, **22**, 661 (1990).
- [14] D. Rivin, *Rubber Chem. Technol.*, **36**, 729 (1964).
- [15] K. Ohkita and N. Tsubokawa, *Carbon*, **10**, 631 (1972).
- [16] M. L. Studebaker, *Proceedings 5th Conference on Carbon II*, Pergamon, New York, 1962, p. 189.
- [17] N. Tsubokawa, A. Kuroda, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1701 (1989).
- [18] N. Tsubokawa, *Ibid.*, **22**, 1515 (1984).
- [19] K. Ohkita, N. Tsubokawa, E. Saitoh, M. Noda, and H. Eguchi, *Nippon Gomu Kyokaishi*, **49**, 900 (1976).
- [20] K. Fujiki, N. Tsubokawa, and Y. Sone, *Tanso*, No. 140, 234 (1989).

Received September 6, 1990

Revision received February 20, 1991