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Initiation Agents

Grafting of Polyester onto Carbon Black

4. Copolymerization of Epoxide with Phthalic Anhydride Initiated by COOK Groups on Carbon Black Surface

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SUMMARY

The grafting of polyesters by the ring-opening copolymerization of epoxides with phthalic anhydride(PhAn) was carried out at 120°C by using carbon black that contained COOK groups as the initiating site of copolymerization. The copolymerization was easily initiated by COOK groups and polyester was effectively grafted onto carbon black: the grafting ratio of polyester obtained from PhAn and glycidyl methacrylate was increased up to about 63% with the increase in conversion. The polyester-grafted carbon black gave a stable colloidal dispersion in chloroform.

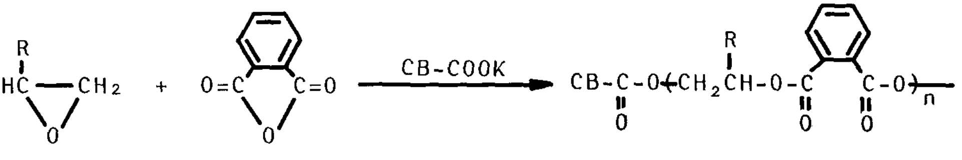
INTRODUCTION

In a series of our papers, β-propiolactone has been reported to polymerize with alkali metal carboxylate groups(COOM; M=Li, Na, K, Rb, or Cs)(1) or quaternary ammonium carboxylate groups($COONR_4$)(2) on the surface of carbon black. It was confirmed that the polyester was propagated from carbon black and effectively grafted onto the surface: for instance, by using COOK groups as catalyst the grafting ratio was increased to 145 % with an increase in conversion. However, neither COOM nor $COONR_4$ groups were able to initiate the ring-opening polymerization of δ-valerolactone or ε-caprolactone.

On the other hand, it has been reported that epoxides are copolymerized with dicarboxylic acid anhydrides by anionic initiators to give the alternating copolymer of the corresponding polyesters(3,4,5).

In this paper, the surface grafting of polyesters by the ring-opening copolymerization of epoxides, such as glycidyl

$$\text{CB-COOH} \xrightarrow{\text{KOH}} \text{CB-COOK}$$



methacrylate(GMA) and styrene oxide(SO), with phthalic anhydride (PhAn) initiated by carbon black that contained COOK groups was described.

EXPERIMENTAL

The carbon blacks used were color-channel blacks FW 200(Degussa A.G.; BET specific surface area, 460 m^2/g), Carbolac 1 (Cabot Corp.; 839.2 m^2/g), and Neospectra II(Columbian Carbon Co.; 906 m^2/g) and furnace black Philblack O(Philips Petroleum Co.; 79.6 m^2/g).

The carbon black containing COOK groups was prepared by the reaction of carboxyl groups with potassium hydroxide according to the method previously reported by us(1).

Glycidyl methacrylate was dried over sodium sulfate and distilled twice under reduced pressure. Styrene oxide(SO) and epichlorohydrin (ECH) were dried over calcium hydride and distilled twice before use. Phthalic anhydride was recrystallized from benzene and then sublimed under reduced pressure. Nitrobenzene used as solvent was purified by the usual method and distilled.

Polymerization was carried out as follows. Under dry nitrogen, freshly distilled epoxide(0.01 mol) was added into a 100-ml teardrop-type flask that contained 0.30 g of carbon black and 0.01 mol of PhAn. When GMA was used as epoxide, 0.01 g of N-phenyl-β-naphthylamine was added to the reaction mixture in order to inhibit the radical polymerization of GMA. The reaction mixture was stirred at 120^0C at a constant rate with a magnetic stirrer. After a definite time, the content of the flask was poured into a large excess of methanol to precipitate the polyester containing carbon black.

The determination of the grafting ratio and the isolation of ungrafted polyester were carried out as follows. To separate the ungrafted polyester from the reaction product, the product was dispersed in chloroform and it was centrifugated at 10^4 rpm until carbon black was precipitated completely. The ungrafted polyester was isolated from the supernatant solution. On the other hand, the carbon black precipitated was extracted with chloroform using a Soxhlet apparatus until no more polymer could be extracted in the refluxing solvent. The grafting ratio and grafting efficiency were determined by using the following equations:

$$\text{Grafting ratio}(\%) = \frac{\text{weight of polymer grafted(g)}}{\text{weight of carbon black used(g)}} \times 100$$

$$\text{Grafting efficiency}(\%) = \frac{\text{weight of polymer grafted(g)}}{\text{weight of total polymer produced(g)}} \times 100$$

RESULTS AND DISCUSSION

Copolymerization of GMA with PhAn Using COOK Groups as Catalyst

It has been reported that alkali metal carboxylates such as sodium acetate initiate the ring-opening copolymerization of epoxides with dicarboxylic acid anhydrides to give polyesters (4). On the other hand, carboxyl groups present on the surface

TABLE 1

Copolymerization of GMA with PhAn under several conditions[a]

No.	Carbon black	GMA (mol)	PhAn (mol)	Conversion (%)
1	None	0.01	0.01	0
2	Neospectra II	0.01	0.01	0
3	COOK-Neospectra II[b]	0.01	-	0
4	COOK-Neospectra II[b]	-	0.01	0
5	COOK-Neospectra II[b]	0.01	0.01	32.0

[a] Experimental conditions: carbon black, 0.30 g; N-phenyl-β-naphthylamine, 0.01 g; nitrobenzene, 3.0 ml; temperature, 120°C; time, 2 h.

[b] The content of COOK groups was 0.40 meqiv/g.

of carbon black are easily neutralized by potassium hydroxide to give potassium carboxylate groups(COOK) quantitatively(6,7).

Therefore, the copolymerization of GMA with PhAn was carried out by the use of carbon black containing COOK groups as initiator under several conditions. The results are shown in Table 1. As shown in Table 1, the copolymerization of GMA with PhAn could not be detected either in the absence of carbon black or in the presence of untreated carbon black of Neospectra II (No. 1,2). Furthermore, neither GMA nor PhAn alone was polymerized by KOH-treated Neospectra II, which contains COOK groups (No. 3,4). On the contrary, when an equimolecular amounts of GMA and PhAn was heated at 120°C, the copolymerization was found to be initiated by COOK-Neospectra II(No. 5).

Figure 1 shows the time-conversion curve of the copolymerization of GMA with PhAn in bulk and in solution of nitrobenzene. It can be seen in Figure 1 that both in bulk and in solution polymerization using 1.0 ml of nitrobenzene, a mild induction period was observed but the rate of the polymerization was very fast after the induction period.

From these results, it is apparent that COOK groups on the surface can initiate the copolymerization of GMA with PhAn.

Catalytic Activity of Various Kinds of Carbon Black with COOK Groups

The copolymerization of GMA with PhAn was carried out by using various kinds of carbon black that contained COOK groups as initiator. The results are summarized in Table 2. The content of COOK groups was estimated from that of carboxyl groups, which was determined according to the method of Rivin (8), because it is known that potassium hydroxide reacts quantitatively with carboxyl groups(6,7).

As shown in Table 2, the initiating activity of these carbon black tends to increase with an increase of COOK groups on

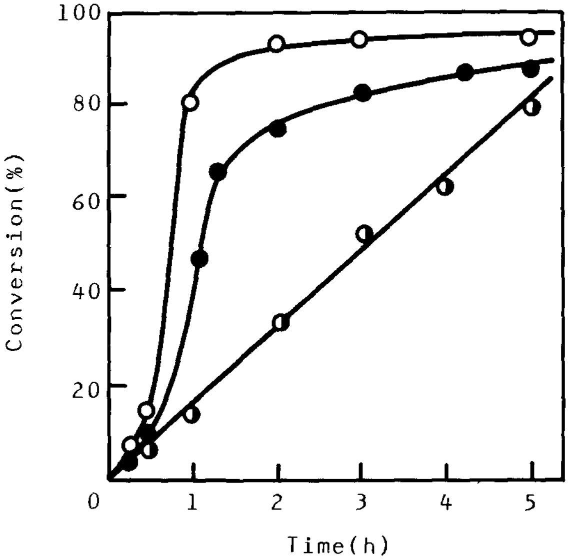


Figure 1. Copolymerization of GMA with PhAn initiated by Neospectra II that contained COOK groups.

COOK-Neospectra II, 0.30 g; GMA=PhAn=0.01 mol; N-phenyl-β-naphthylamine, 0.01 g; temperature, 120°C: (○) bulk; (●) nitrobenzene, 1.0 ml; (◐) nitrobenzene, 3.0 ml.

TABLE 2

Copolymerization of GMA with PhAn Initiated by Various Kinds of Carbon Black Containing COOK Groups[a]

Carbon black	COOK groups (mequiv/g)	Conversion (%)
Neospectra II[b]	0	0
COOK-Neospectra II[b]	0.40	32.0
COOK-Carbolac 1[b]	0.54	40.0
COOK-FW 200[b]	0.61	40.3
COOK-Philblack 0[c]	0	0.3

[a] Experimental conditions: carbon black, 0.30 g; GMA=PhAn=0.01 mol; N-phenyl-β-naphthylamine, 0.01 g; nitrobenzene, 3.0 ml; temperature, 120°C; time, 2 h.

[b] Color-channel black.

[c] Furnace black.

the carbon black surface. Potassium hydroxide-treated Philblack O scarcely had an ability to initiate the copolymerization. This is explained by the fact that Philblack O contains no carboxyl groups. The result indicates that it is not necessary to take into account the initiation by potassium hydroxide adsorbed on the surface of carbon black.

Proof of Grafting onto Carbon Black

The carbon black obtained from the copolymerization gave a stable colloidal dispersion in a good solvent for polyester. This phenomenon suggests that polyester has been grafted onto the carbon black.

Figure 2 shows the relationship between conversion and the grafting ratio and grafting efficiency of the polyester obtained from the copolymerization of GMA with PhAn. It was found that the polyester was grafted onto the surface and the grafting ratio gradually increased with an increase in conversion. The value of the grafting ratio was lower than that obtained from anionic ring-opening polymerization of β-propiolactone(1) but much higher than that obtained from radical polymerization of vinyl monomers(9). In addition, the grafting efficiency was high during the first few percents of conversion but decrease with the increase in conversion. The result indicates that the grafted polyester is propagated from COOK groups and that the ungrafted polyester is gradually formed by a chain transfer reaction of growing polymer anion.

Characterization of the Ungrafted Polyester

The ungrafted polymer obtained from the copolymerization of GMA with PhAn was identified as the expected polyester(cf. reaction scheme; $R=-CH_2OCOC(CH_3)=CH_2$) by IR and NMR spectra: IR(KBr):1730(vs;C=O), 1630(m;C=C), 1125(s;C-O-C),and 1070 cm^{-1} (s;C-O-C). NMR($CDCl_3$): $\delta=1.85(3H,-C\underline{H}_3)$, $4.43(4H,-C\underline{H}_2-O-)$, $5.48(2H,=C\underline{H}_2)$, $6.05(1H,>C\underline{H}-)$, and 7.53 ppm(4H,aromatic).

On the other hand, it was confirmed that not only the ungrafted polyester but also polyester-grafted carbon black could be cross-linked with vinyl monomers, such as styrene, in the presence of benzoyl peroxide at 80°C. Such cross-linking reaction of polyester-grafted carbon black is of interest in connection with an application of carbon black-polymer composite.

Figure 3 shows the relationship between conversion and the intrinsic viscosity of the ungrafted polyester. It was found that the intrinsic viscosity is about 0.035 dl/g(chloroform, 30.0°C) regardless of its conversion.

Grafting of Polyesters from Several Epoxides and Dicarboxylic Acid Anhydrides

The copolymerization of several epoxides with dicarboxylic acid anhydrides was carried out at 120°C by using COOK groups as catalyst and the grafting of the polyesters was evaluated. The results are summarized in Table 3.

From the results shown in Table 3, it is apparent that COOK groups have an ability to initiate the copolymerization of epoxides with dicarboxylic acid anhydrides and that various kinds of polyester can be grafted onto carbon black surface.

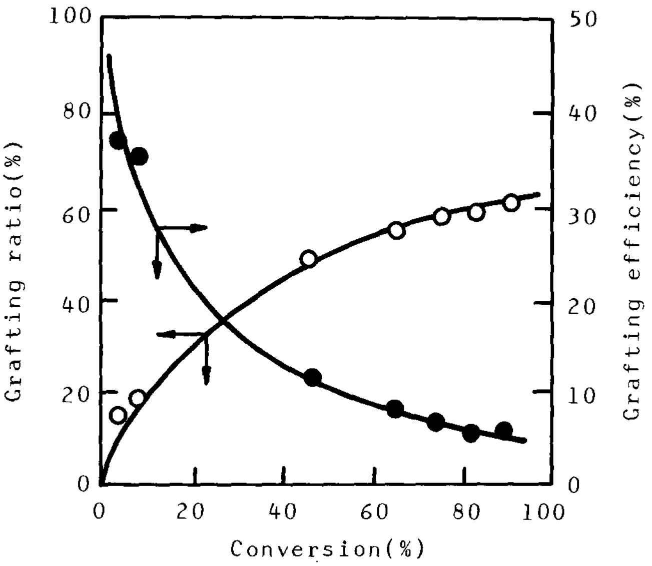


Figure 2. The relationship between conversion and grafting ratio(grafting efficiency).

COOK-Neospectra II, 0.03 g; GMA=PhAn=0.01 mol; N-phenyl-β-naphthylamine,0.01 g; nitrobenzene, 1.0 ml; temperature, 120°C.

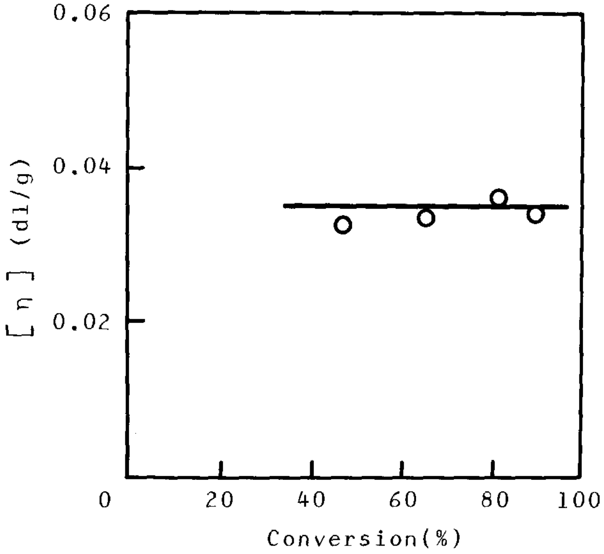


Figure 3. Effect of conversion on the intrinsic viscosity of ungrafted polyester formed.

COOK-Neospectra II, 0.30 g; GMA=PhAn=0.01 mol; N-phenyl-β-naphthylamine,0.01 g; nitrobenzene, 3.0 ml; temperature, 120°C.

TABLE 3

Grafting of Polyesters from Epoxides and Dicarboxylic Acid Anhydrides onto Carbon Black[a]

Epoxide	Anhydride	Conversion (%)	Grafting ratio (%)
GMA	PhAn	46.5[b]	52.0
GMA	MaAn[c]	80.0[b]	105.0
SO	PhAn	25.2	43.3
SO	MaAn[c]	18.4	53.5
ECH	PhAn	44.2	23.2

[a] Experimental conditions: COOK-Neospectra II, 0.30 g; epoxide=dicarboxylic acid anhydride=0.01 mol; temperature, 120°C; time, 1 h.

[b] Solution polymerization(nitrobenzene, 1.0 ml).

[c] Maleic anhydride.

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