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Grafting of Polyesters onto Carbon Black

2. Effect of Temperature and Solvent on the Polymerization of β-Propiolactone Initiated by COOK Groups on the Surface of Carbon Black

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SUMMARY

The effect of temperature and solvent on the polymerization of β-propiolactone initiated by carbon black containing potassium carboxylate groups (COOK) was investigated. The rate of the polymerization (Rp) was found to increase with a rise in temperature. On the other hand, Rp varied with the solvents in the following order: toluene < chloroform << N,N-dimethylformamide (DMF). This order was in agreement with that of increasing dielectric constant of the solvents. Furthermore, it was found that the grafting ratio of the polyester onto the surface of carbon black and the molecular weight of the homopolymer formed decreased, depending on the solvents used, in the following order: toluene > chloroform > DMF.

INTRODUCTION

In the previous paper, we reported that carbon black containing alkali metal carboxylate groups (COOM; M= Li, Na, K, Rb, or Cs) had an ability to initiate the anionic ring opening polymerization of β-propiolactone (PL) and polyester grafted effectively onto the surface of carbon black (TSUBOKAWA et al. 1982, TSUBOKAWA et al. to be published).

$$\text{CB-COOH} \xrightarrow{\text{MOH}} \text{CB-COO}^-\text{M}^+ \xrightarrow{\text{PL}} \text{CB-COOCH}_2\text{CH}_2\text{COO}^-\text{M}^+$$

$$\xrightarrow{\quad} \xrightarrow{\text{nPL}} \xrightarrow{\quad} \text{CB-COO}\left(\text{CH}_2\text{CH}_2\text{COO}\right)_n\text{CH}_2\text{CH}_2\text{COO}^-\text{M}^+$$

Furthermore, the rate of polymerization and the grafting ratio of the polyester were found to be markedly affected by the ionic nature (electropositivity) of the alkali metal countercation. In such polymerization system, it was confirmed that the grafted polyester was propagated from COO^-M^+ groups on the surface of carbon black and then homopolymer gradually formed by chain transfer reaction of the growing polymer anion

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to the monomer.

It is expected that the propagation and chain transfer of growing chain is affected by polymerization conditions. Therefore, the effect of temperature and solvent on the propagation and chain transfer becomes an interesting problem for the preparation of polyester-grafted carbon black with higher grafting ratio.

In the present paper, the effect of temperature and solvent on the polymerization of PL initiated by COOK groups on the surface of carbon black was investigated.

EXPERIMENTAL

The carbon black used was color channel black FW 200 (BET specific surface area, 460 m^2/g; carboxyl groups, 0.61 meq/g).

The purification of PL, the preparation of carbon black containing COOK groups, polymerization procedures, and the determination of grafting ratio were as previously described in detail (TSUBOKAWA et al. to be published).

The intrinsic viscosity of homopolymer was determined in chloroform solution at 30.0°C.

Toluene, chloroform, and N,N-dimethylformamide (DMF) were used as solvents. Toluene was washed with concentrated H_2SO_4, water, aqueous NaOH, and water, dried over $CaCl_2$, and distilled over metalic sodium. Chloroform was washed with concentrated H_2SO_4, water, aqueous Na_2CO_3 and water, dried over $CaCl_2$, and distilled over phosphorus pentoxide. N,N-dimethylformamide was dried over CaH_2 and fractionally distilled in vacuo under nitrogen.

RESULTS AND DISCUSSION

Effect of Temperature on the Polymerization

By use of 5.73g of PL and 0.3g of FW 200 containing COOK groups (COOK-FW 200), the bulk polymerization was carried out at 30, 50, and 70°C, and the results are shown in Figure 1. The rate of the polymerization was found to increase with a rise in temperature.

The Arrhenius plots for the above results gave a straight line and apparent activation energy of the polymerization was estimated to be 11 kcal/mol. The value is somewhat larger than that of ordinary anionic ring opening polymerization of β-lactones (BIGDELI and LENZ 1978, LENZ 1981).

Effect of Temperature on Grafting Ratio and Molecular Weight of Homopolymer

As mentioned above, in such polymerization system, polyester formed was grafted onto the surface of carbon black.

In order to obtain a polyester-grafted carbon black with higher grafting ratio, it is necessary to control the chain transfer reaction. Therefore, the effect of temperature on

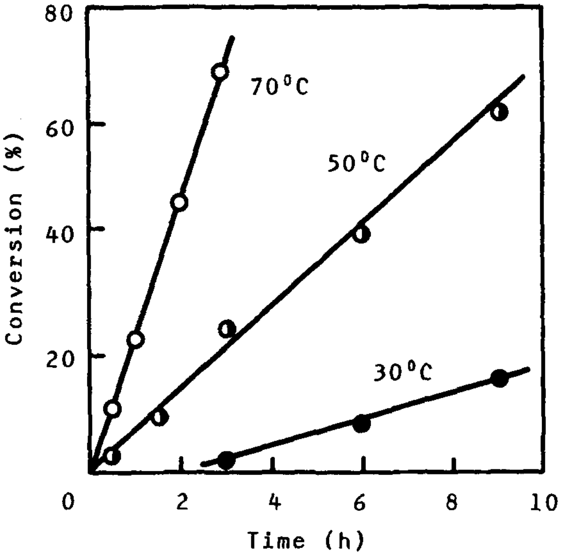

Figure 1. Dependence of temperature on the polymerization of PL initiated by FW 200 containing COOK groups. COOK-FW 200, 0.3g; PL, 5.73g.

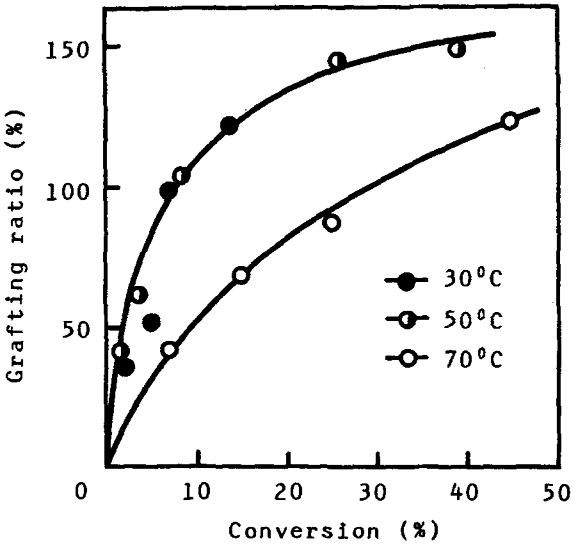

Figure 2. Dependence of temperature on grafting ratio. COOK-FW 200, 0.3g; PL, 5.73g.

the grafting ratio of polyester was investigated. The results are shown in Figure 2. As shown in Figure 2, at each temperature, the grafting ratio increased with an increase of conversion. In addition, it is apparent that the grafting ratio onto carbon black obtained at 30 and 50°C is larger than that obtained at 70°C. Namely, the results indicate that when the polymerization was carried out at 70°C, much homopolymer was formed in comparison with the polymerization at 30 and 50°C.

On the other hand, Figure 3 shows the effect of temperature on the intrinsic viscosity of the homopolymer obtained from the above polymerization. As is seen in Figure 3, the intrinsic viscosity of the homopolymer decreased, depending on the temperature, in the following order: 30°C > 50°C > 70°C.

These results are explained as follows. The grafted polyester is propagated from COOK groups on the surface of carbon black. Then, increasing temperature of the polymerization will cause an increase in the rate of chain transfer reaction of the growing chains to the monomer (YAMASHITA et al. 1963). Accordingly, when the polymerization was carried out at 70°C, lower grafting ratio and the homopolymer of lower molecular weight will be formed.

Effect of Solvent on the Polymerization

By use of toluene (dielectric constant; 2.38), chloroform (4.70), and DMF (36.71) as solvents, the effect of solvent on the rate of the polymerization of PL was studied.

From the result shown in Figure 4, it is indicated that the rate of the polymerization increased, depending on the solvents used, in the following order: toluene < chloroform << DMF. The polymerization was markedly accelerated in DMF. This order is in agreement with that of increasing dielectric constant of these solvents.

The effect of solvent on the anionic ring opening polymerization of PL was investigated by Kagiya et al. (KAGIYA et al. 1965). Furthermore, the similar effect of solvent on the anionic polymerization of styrene was reported by O'Driscoll et al. and Welch (O'DRISCOLL and TOBOLSKY 1959, WELCH 1960). They described that the solvation of countercation by solvents will increase the effective charge of the carbanion of propagating end, and the subsequent increase in the rate constant of propagation.

Accordingly, the effect of solvent on the polymerization of PL is explained as follows. The growing chains are ion pairs such as $\mathrm{CB{\sim\sim\sim}COO^{-}K^{+}}$. The increasing dielectric constant of the solvents will cause an increase in separation of the ion pairs by the solvation of countercation (K^{+}). Thus increasing charge separation of the ion pairs increase the effective negative charge of carboxylate anion (propagating anion), and then can cause an increase in the rate of the polymerization (SZWARC 1960).

Effect of Solvent on Grafting Ratio and Molecular Weight of Homopolymer

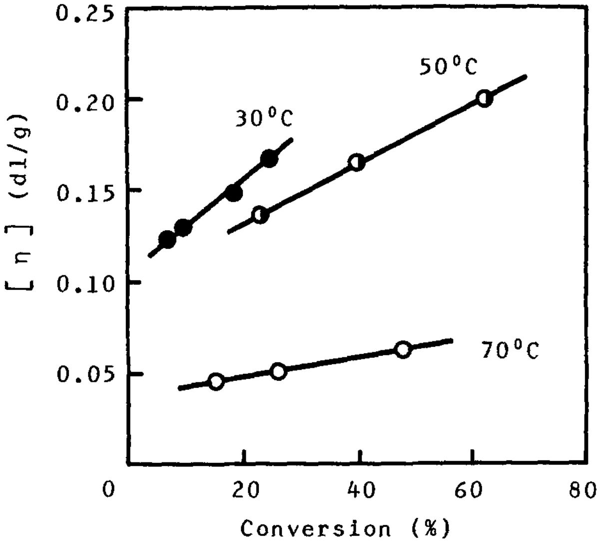

Figure 3. Dependence of temperature on intrinsic viscosity of the homopolymer.
COOK-FW 200, 0.3g; PL, 5.73g.

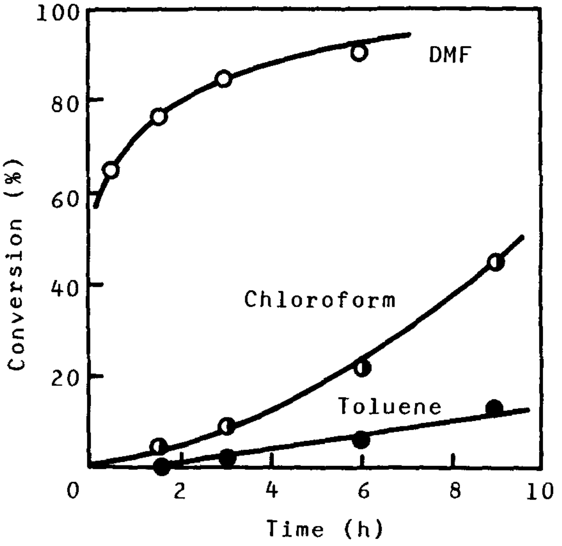

Figure 4. Dependence of solvent on the polymerization.
COOK-FW 200, 0.3g; PL, 5.73g; Solvent, 10.0ml; Temp. 50°C.

As described above, the dielectric constant of solvent had a remarkable effect on the rate of the polymerization of PL initiated by COOK groups on the surface. The second problem is the effect of solvent on the grafting ratio and the molecular weight of the homopolymer. Therefore, the effect of solvent on the grafting ratio was investigated.

The results are shown in Figure 5. It is apparent that the grafting ratio of the polyester onto the surface obtained by the above polymerization varied with the solvents in the following order: toluene > chloroform > DMF. This order is in agreement with that of increasing dielectric constant of the solvents.

Furthermore, Figure 6 shows the effect of solvent on the intrinsic viscosity of the homopolymer. The result shows that the molecular weight of the homopolymer is decreased when the dielectric constant of the solvent is increased. Namely, DMF with the highest dielectric constant gave the polymer of the lowest molecular weight.

On the other hand, Zilkha et al. reported that in the system of the anionic polymerization of acrylonitrile, the molecular weight of poly(acrylonitrile) formed decreased with an increase in the dielectric constant of the solvents (ZILKHA and KATZ 1962).

Accordingly, these phenomena will be explained as follows. As mentioned above, the polyester is propagated from COOK groups on the surface of carbon black and the increasing dielectric constant of the solvent increase the negative charge of the carboxylate anion of the propagating end by solvation. Thus the increasing negative charge of the propagating anion will lead to a greater attraction of the α-hydrogen of the monomer (chain transfer reaction). As a result , the polyester of lower molecular weight and lower grafting ratio will be obtained when solvent with higher dielectric constant such as DMF was used.

CONCLUSIONS

It became apparent that the rate of the polymerization of PL initiated by COOK groups on the surface of carbon black was markedly affected by the temperature of polymerization and the dielectric constant of solvent. The increasing temperature increased the rate of the polymerization, but decreased the grafting ratio of polyester onto the surface.

On the other hand, the rate of the polymerization increased as the dielectric constant of the solvent increased. In addition, the grafting ratio of polyester onto the surface and the molecular weight of homopolymer decreased with an increase in the dielectric constant of solvents. These phenomena were due to the increasing solvation of countercation by solvents when the dielectric constant of solvents increased.

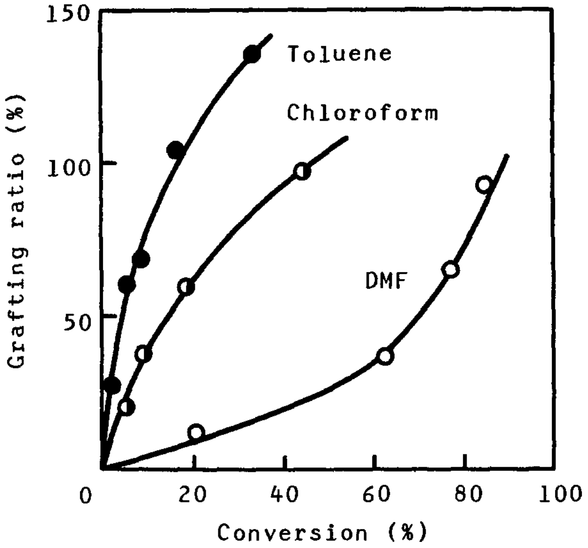

Figure 5. Dependence of solvent on grafting ratio. COOK-FW 200, 0.3g; PL, 5.73g; Solvent, 10.0ml; Temp. 50°C.

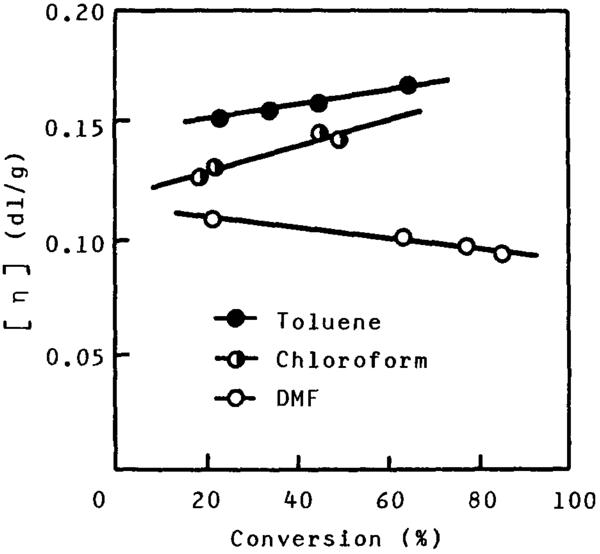

Figure 6. Dependence of solvent on intrinsic viscosity of the homopolymer.
COOK-FW 200, 0.3g; PL, 5.73g; Solvent, 10.0ml; Temp. 50°C.

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