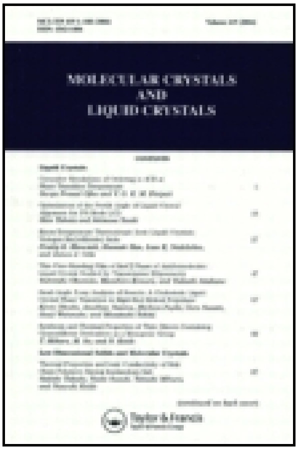

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On the Interaction between Alkali Metal-GICs and Unsaturated Hydrocarbons

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RbC_{24} and CsC_{24} were allowed to react with isoprene, styrene or 1,3-butadiene. RbC_{24} expanded slowly along the c-axis direction through contact with these unsaturated hydrocarbons. Monomer molecules are considered to be introduced into the interlayer of RbC_{24} and polymerized. In the case of CsC_{24}, isoprene was polymerized in a similar manner as RbC_{24} and KC_{24}, whereas the reactivity of styrene and 1,3-butadiene was low. The different reactivities are explained on the basis of the activity of polymerization initiators. The reactivity of monomers to polymerize in a certain GIC is in the following order: isoprene > 1,3-butadiene > styrene, which is the reverse order of reactivity recognized in the conventional polymerization.

Keywords: intercalation; alkali metal; unsaturated hydrocarbons

INTRODUCTION

The chemical reaction in the interlayer spacing of graphite has been a subject of interest during recent years. It is known that some organic molecules, which are co-intercalated into graphite intercalation compounds (GICs) with alkali metals, react in the interlayer spacing of graphite[1,2]. Especially when unsaturated hydrocarbons are co-intercalated, they are found to be polymerized within the interlayer spacing of the alkali metal-GICs. For a few organic molecules such as benzene[3-5] or ethylene[6,7] the oligomerization process and the product have been studied in detail. In the previous paper[8,9] we reported the interaction between the potassium-GIC and unsaturated hydrocarbons. After contact with isoprene, styrene and 1,3-butadiene, KC_8 and KC_{24} expanded along the c-axis direction. This is due to the polymerization of unsaturated hydrocarbons in the interlayer spacing of graphite. The present work describes the interaction between stage 2 alkali metal-GICs, RbC_{24} and CsC_{24}, and unsaturated hydrocarbons.

EXPERIMENTAL

Slabs (5×1×0.25mm, *ca.* 2.5mg) of Union Carbide HOPG were used as the starting material. For preparation of RbC_{24} and CsC_{24} the conventional two-bulb method was employed. The graphite temperature Tg was maintained at 420 ℃ and the intercalate temperature Ti at 200℃ for RbC_{24} and Tg at 520℃ and Ti at 195℃ for CsC_{24}.

A sample of RbC_{24} or CsC_{24} was transferred to a reaction chamber of Pyrex glass in vacuo through a glass break-seal, for it to react with unsaturated hydrocarbons. The detail of this procedure is shown in the previous paper[9].

The reaction products were characterized by X-ray powder diffractometry (Rigaku, LINT-1500) and thermogravimetry in a nitrogen stream (MAC Science, TG-DTA 2000).

RESULTS AND DISCUSSIONS

After contact with the vapour of isoprene, styrene or 1,3-butadiene, RbC_{24} expanded slowly along the c-axis direction. This phenomenon and the products formed therein are identical to those observed in the interaction of potassium-GICs, KC_8 and KC_{24}, with the same kind of unsaturated hydrocarbons[9]. Black colour product resembles exfoliated graphite in shape, but the bulk density is almost identical to the commercially available polyisoprene, polystyrene or polybutadiene. Molecules of unsaturated hydrocarbons are considered to be introduced into the interlayer spacing of RbC_{24} and polymerized progressively. X-ray powder diffraction patterns of the products from RbC_{24} and unsaturated hydrocarbons are shown in Fig. 1. No diffraction line for graphite or GIC was observed, and the broad peaks resemble the

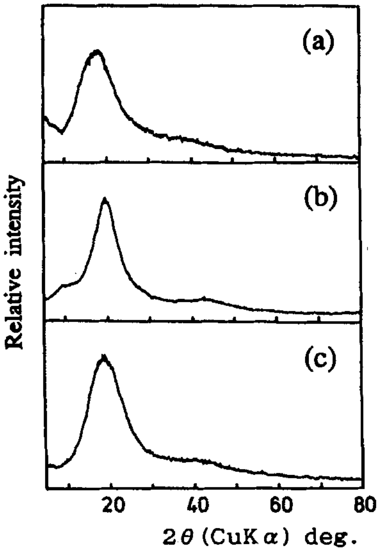

Fig. 1 X-ray powder diffraction patterns of products from the reaction of RbC_{24} with *ca.* 1 g of (a) isoprene, (b) styrene and (c) 1,3-butadiene.

patterns of commercially available polyisoprene, polystyrene and polybutadiene. The curves of thermogravimetry (TG) and differential thermal analysis (DTA) with respect to the products are also quite similar to those for the control polyisoprene, polystyrene and polybutadiene. An example is shown in Fig. 2 (a).

The expansion of lattice of RbC_{24} depends on the introduction of the unsaturated hydrocarbon into the interlayer spacing of RbC_{24}. The introduced monomer is considered to be under the influence of the negatively charged graphite layer of RbC_{24} to initiate anionic polymerization. The detail of this mechanism is described in the previous paper[9].

Taking this mechanism into account, we propose a schematic diagram of the GIC-initiated polymerization, which is shown in Fig. 3. This schematic model of the product suggests that the stacked graphite layers are drawn apart, which gives no diffraction line of graphite or GIC.

The products from the reaction of CsC_{24} with isoprene is identical

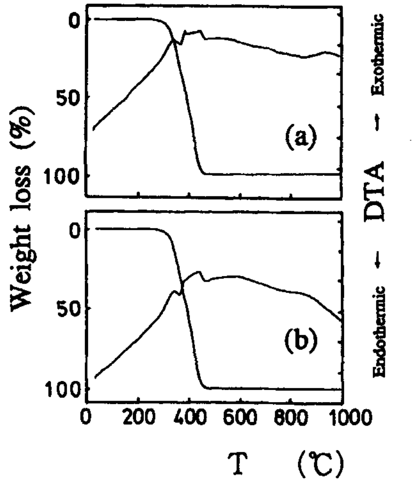

Fig.2 TG and DTA curves of products from the reaction of isoprene with (a) RbC_{24} and (b) CsC_{24}.

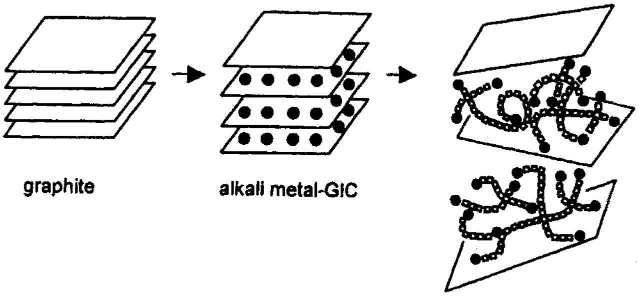

Fig.3 Schematic diagram showing the GIC-initiated polymerization: (●) alkali metal; (□)unsaturated hydrocarbon.

to those from the reactions of KC_8, KC_{24} and RbC_{24}: the X-ray powder diffraction pattern of this product is shown in Fig. 4 (a). However, in the reaction of CsC_{24} with styrene or 1,3-butadiene, the reactivity of the monomer was low. The amounts of fixed styrene and 1,3-butadiene in ca. 3.7 mg of CsC_{24} were ca. 0.5 mg and ca. 130 mg, respectively. The polymerization proceeded in two days, but no more change was observed in subsequent 20 days. In the X-ray powder diffraction patterns, shown in Fig. 4 (b) and (c), the characteristic broad

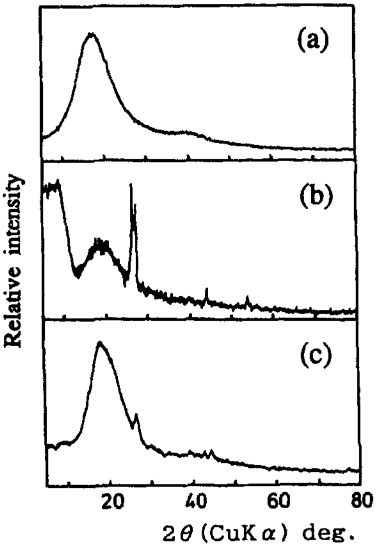

Fig.4 X-ray powder diffraction patterns of products from the reaction of CsC_{24} with (a) ca. 1 g of isoprene, (b) ca. 0.5 mg of styrene and (c) ca. 130 mg of 1,3-butadiene.

peak of the polymers with an unknown peak is observed. The latter can be regarded as the peak of high stage Cs-GICs. The weak intensity of the polymer peak and the presence of the latter peak suggest that the extent of GIC-initiated polymerization (Fig. 3) is low. The reactivities are explained maybe related to the activity of polymerization initiators. The degree of charge-transfer from alkali metal to graphite basal plane in the GICs of Rb and K is higher than that of Cs[10], which gives the higher activity of RbC_{24} and KC_{24} as a polymerization initiator.

The reactivity of monomers to polymerize in CsC_{24} follows the order:

isoprene > 1,3-butadiene > styrene,

which is the reverse of reactivity observed with conventional polymerization. This peculiar order could be attributed to the fact that the polymerization takes place via two-dimensional opening where influence from the graphite layer is expected to be strong. Further studies are necessary to reveal more details about the reactivity of monomers. Work is in progress to elucidate this bahaviour.

References

[1] J. Jegoudez, C. Mazieres and R. Setton, *Synth. Met.*, **7,** 85 (1983).

[2] R. Setton, in *Graphite Intercalation Compounds I, Structure and Dynamics,* edited by H. Zabel and S. A. Solin (Springer Verlag, Berlin, 1990), p305.

[3] G. Merle and F. Beguin, *Carbon,* **18,** 371 (1980).

[4] S. Matsuzaki and M. Sano, *Chem. Phys. Lett.,* **115,** 424 (1985).

[5] S. Matsuzaki, M. Taniguchi and M. Sano, *Synth. Met.,* **16,** 343 (1986).

[6] Y. Takahashi, K. Oi, T. Terai and N. Akuzawa, *Carbon,* **29,** 283 (1991).

[7] H. Pilliere, Y. Takahashi, T. Yoneoka, T. Otosaka and N. Akuzawa, *Synth Met.,* **59,** 191 (1993).

[8] H. Shioyama, *Carbon,* **35,** 1664 (1997).

[9] H. Shioyama, K. Tatsumi, N. Iwashita, K. Fujita and Y. Sawada, *Synth. Met.,* **96,** 229 (1998).

[10] N. Gunasekara, T. Takahashi, F. Maeda, T. Sagawa and H. Suematsu, *Z. Phys.,* **B70,** 349 (1988).