

Polymerization in the interlayer of KC_{24} in the presence of organic solvents

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KC_{24} was allowed to react with an unsaturated hydrocarbon–organic solvent mixture. Isoprene molecules were introduced into the interlayer of KC_{24} and polymerized, whereupon organic solvents such as cyclohexane, hexane, 2,5-dimethyltetrahydrofuran, benzene, toluene and *m*-xylene were incorporated into the polyisoprene. A similar incorporation was observed when styrene was polymerized in the interlayer in the presence of aromatic solvents. On the other hand, the polymerization of styrene was carried out in the interlayer without the incorporation of aliphatic solvents. This is explained on the basis of the low affinity of aliphatic solvents for aromatic styrene and for graphene layers.

1 Introduction

Graphite intercalation compounds (GICs) are of interest to chemists and physicists because of their unusual properties. Much attention has been focused on the preparation and the properties of GICs themselves and on their utilization.^{1,2} In recent years, the chemical reaction in the interlayer spacing of graphite has been a subject of interest. Because environmental factors of the chemical reaction are peculiar, *i.e.* the reaction occurs in a two-dimensional opening where a strong influence from the adjoining graphene layer is expected, novel reaction products are thus expected. In a previous paper we reported the reduction of metal chloride in the interlayer.^{3–5}

Organic reactions in the interlayer spacing of graphite have been also studied.⁶ Especially when unsaturated hydrocarbons are co-intercalated, they are found to be polymerized within the interlayer spacing of the alkali metal-GICs. We reported recently that isoprene, styrene or 1,3-butadiene can be introduced into the interlayer spacing of GICs such as KC_8 , KC_{24} , RbC_{24} and CsC_{24} and polymerized progressively.^{7–10} The product of this reaction is a composite obtained by delamination of graphite to graphene sheets and dispersion in a continuous polymer matrix (delaminate hybrid).¹¹

The present work describes the reaction of KC_{24} with solutions of unsaturated hydrocarbons in organic solvents. When monomer molecules were introduced into the interlayer of KC_{24} and polymerized, some organic solvents were incorporated into the polymer. On the other hand, polymerization in the interlayer was carried out without the incorporation of organic solvent in certain combinations of monomer and organic solvent.

2 Experimental

Slabs ($5 \times 1 \times 0.25$ mm, *ca.* 2.5 mg) of highly oriented pyrolytic graphite (HOPG) from Advanced Ceramics Corp. were used as the starting materials. The conventional two-bulb method was employed for the preparation of KC_{24} . The reaction tube of Pyrex glass was sealed under vacuum and placed in a two-zone furnace for 4 days. The temperatures were maintained at $T_g = 410^\circ\text{C}$ for the graphite and $T_i = 250^\circ\text{C}$ for the intercalate. During this intercalation process, black HOPG turned blue.

A sample of KC_{24} (*ca.* 2.8 mg) was transferred *in vacuo* to a reaction chamber of Pyrex glass through a glass break-seal, to

be immersed in mixtures of the unsaturated hydrocarbon (*ca.* 1.5 ml) and organic solvent (*ca.* 1.5 ml). The unsaturated hydrocarbons isoprene and styrene, and the organic solvents cyclohexane, hexane, 2,5-dimethyltetrahydrofuran, benzene, toluene and *m*-xylene were deaerated by repeated freeze–pump–thaw cycles, dehydrated using molecular sieve 4 Å and were purified by vacuum distillation.

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

3 Results and discussion

3.1 Aliphatic solvents

A small slab of KC_{24} immersed in the mixture of isoprene and hexane was found to have expanded along the *c*-axis direction. The expansion proceeded slowly for several hours until the entire mixed solution was incorporated into the black coloured product (the starting KC_{24} is shiny blue). In previous papers,^{7–10} we reported that the introduced monomer of isoprene or styrene is considered to be under the influence of the negatively charged graphene layer of KC_{24} and the anionic polymerization starts. The initiator in this system is the negatively charged graphene layers. The same kind of polymerization is considered to proceed in the interlayer when KC_{24} is allowed to react with an isoprene–hexane mixture. The morphology of the product suggests that uptake of hexane accompanied the polymerization of isoprene in the interlayer. A similar product was obtained when KC_{24} was immersed in isoprene–cyclohexane or isoprene–2,5-dimethyltetrahydrofuran mixtures (Table 1).

When styrene is chosen as the unsaturated hydrocarbon, the immersion of KC_{24} into unsaturated hydrocarbon–aliphatic solvent mixtures leads to different products. The polymerization reactivity of styrene in the interlayer of graphite is lower than that of isoprene, which is the reverse of the reactivity observed in conventional polymerization,⁹ and hence, an expansion of KC_{24} was not observed in styrene–cyclohexane mixtures. On the other hand, slow expansion of KC_{24} was observed in styrene–hexane or styrene–2,5-dimethyltetrahydrofuran mixtures. This expansion stopped when the growth of the black product amounted to half of the mixture and a liquid with low viscosity remained.

An example of an X-ray powder diffraction pattern of the

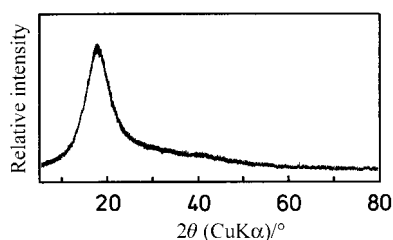
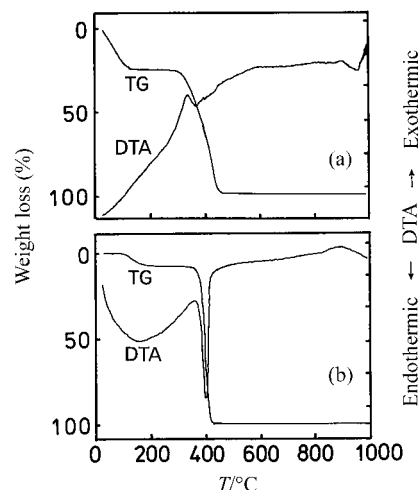
Table 1 Appearance of the products

Solvent	Monomer	
	Isoprene	Styrene
Cyclohexane	A	No reaction
Hexane	A	B
2,5-Dimethyltetrahydrofuran	A	B
Benzene	A	A
Toluene	A	C
<i>m</i> -Xylene	A	C

A: Homogeneous polymer of a black colour. B: Black polymer formed in the bottom of the liquid. C: Black polymer with a small amount of viscous liquid.

product obtained by the immersion of KC_{24} in an isoprene–aliphatic solvent mixture is shown in Fig. 1. No diffraction line for GIC or graphite was observed, and the broad peak with a shoulder resembles the pattern of commercially available polyisoprene and that of the product from the reaction of KC_{24} (*ca.* 2.8 mg) with pure isoprene (*ca.* 1.5 ml). These mean that the regularity in the crystal structure of KC_{24} or graphite disappeared with the development of polyisoprene in the interlayer, and hence, the broad peak of polyisoprene was solely observed. The coexistence of the aliphatic solvent in polyisoprene was in any event not proved by XRD. The curves of thermogravimetry (TG) and differential thermal analysis (DTA) with respect to the products from the reaction of KC_{24} in isoprene–hexane and styrene–hexane mixtures are shown in Fig. 2. TG and DTA curves of the product from the KC_{24} –styrene–hexane system [Fig. 2(b)] are quite similar to those for the product from the reaction of KC_{24} with styrene only, considering also a small weight loss observed between about 80 and 160 °C. The polymer was reported to be completely removed by vaporization or decomposition at about 400 °C, and that the residue originated from the HOPG.⁸ In contrast, a characteristic weight loss between room temperature (RT) and 120 °C [Fig. 2(a)] suggests that hexane incorporated in the polyisoprene matrix was liberated. The ratio of weight loss at the temperatures between RT and 120 °C to that between 320 and 440 °C does not reflect the composition of hexane and polyisoprene. This is because a weight loss of the product due to the liberation of hexane took place even at room temperature before loading the sample into the apparatus for TG and DTA measurements. The DTA curve in Fig. 2(a) suggests an endothermic process at temperatures between RT and about 150 °C. The endothermic propensity at these temperatures is not observed in Fig. 2(b) and this process might be attributable to the liberation of hexane.

Aliphatic solvents used in the experiments do not co-intercalate into the interlayer of KC_{24} , as was reported by Abe *et al.*¹² and also confirmed by our preliminary investigation. Such aliphatic solvents were incorporated into polyisoprene when the polymerization took place in the interlayer spacing of KC_{24} . In contrast, the incorporation was not observed if styrene was used as a monomer. This difference is possibly

**Fig. 1** X-Ray powder diffraction pattern of the product obtained by the immersion of KC_{24} in an isoprene–cyclohexane mixture.**Fig. 2** TG and DTA curves of products from the reaction of KC_{24} in (a) isoprene–hexane and (b) styrene–hexane.

attributed to the affinity of the solvent molecule for isoprene or styrene. Aliphatic solvents have an affinity for aliphatic isoprene, and hence incorporation into polyisoprene was observed, whereas styrene polymerized in the interlayer without incorporation because the affinity of aromatic styrene for aliphatic solvents is not as strong. Such a phenomenon is often observed in conventional polymerization, and organic solvents are classified as good or poor according to whether they are incorporated into the polymer or not.

3.2 Aromatic solvents

A combination of aliphatic isoprene and aromatic solvents such as benzene, toluene and *m*-xylene would not result in so good an affinity, and a separation of solvents is predicted. To the contrary, when KC_{24} was immersed in the mixture of isoprene and aromatic solvent, the entire solution was incorporated into the product. XRD patterns and TG and DTA curves of the product are quite similar to those of the product from the KC_{24} –isoprene–hexane system. Benzene and toluene molecules are known to be co-intercalated into KC_{24} .¹ However, this is not the main reason for the incorporation, because *m*-xylene is not co-intercalated into KC_{24} . Co-intercalated monomeric isoprene is considered to be under the influence of the negatively charged graphene layer of KC_{24} , and anionic polymerization starts, initiated by electron transfer from graphene layers to the monomer.⁸ As aromatic solvents might have a certain affinity for graphene layers, they find easy access to the sites where the polymerization proceeds. This might be one possible explanation for the incorporation. It should be emphasized again that the incorporation is determined not only by the affinity of the solvent for monomer but also by the affinity of the solvent for graphene layers in the vicinity of which the active sites of the polymerization exist.

In the case of the polymerization of aromatic styrene in the interlayer, the incorporation of aromatic solvents is expected. As the polymerization reactivity of styrene is low in the interlayer of graphite, the expansion of KC_{24} proceeded only very slowly. The expansion stopped after about one week, and one tenth of the solution remained. The viscosity of this residual solution was high, because styrene polymerized spontaneously during this week in the bulk solution, and hence further polymerization in the interlayer did not take place. Nevertheless, the polymerization of styrene in the interlayer was found to promote fundamentally the incorporation of benzene, toluene or *m*-xylene.

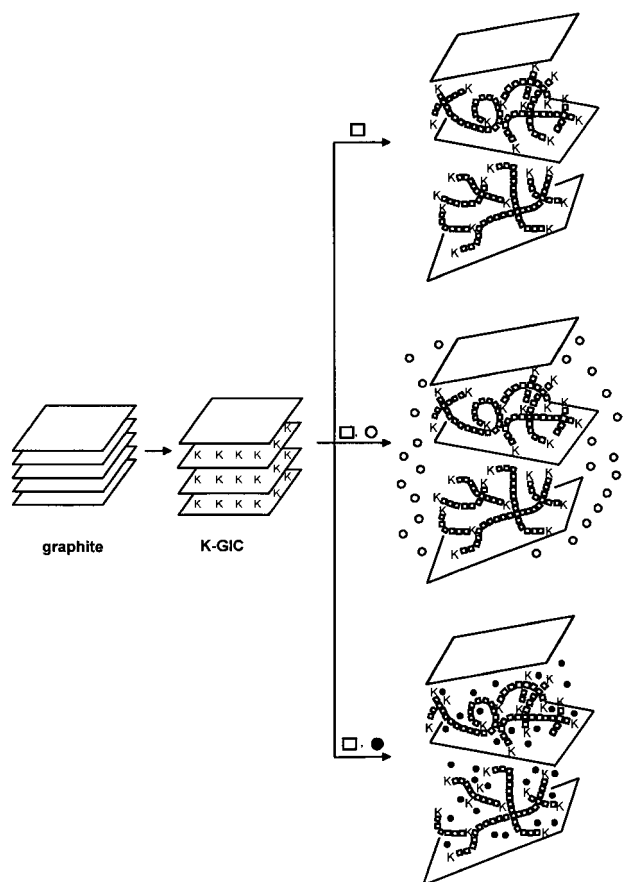


Fig. 3 Schematic diagram showing the GIC-initiated polymerization in the interlayer: (K) potassium; (□) unsaturated hydrocarbon; (●) good solvent; (○) poor solvent.

4 Conclusion

KC₂₄ was allowed to react with the unsaturated hydrocarbon–organic solvent mixtures. Aliphatic isoprene was introduced

into the interlayer of KC₂₄ and polymerized, whereupon aliphatic organic solvents such as cyclohexane, hexane and 2,5-dimethyltetrahydrofuran were occluded in the polyisoprene. On the other hand, the polymerization of aromatic styrene in the interlayer occurred without the incorporation of aliphatic solvents. This difference is explained on the basis of the affinity of the solvent for the unsaturated hydrocarbon. Aliphatic solvents are good solvents for isoprene and incorporation was observed, whereas they have poor affinity for styrene and hence no incorporation was observed. This is illustrated schematically in Fig. 3. In the case of aromatic solvents such as benzene, toluene and *m*-xylene, the incorporation was observed when both aliphatic isoprene and aromatic styrene were polymerized in the interlayer, because aromatic solvents might have a certain affinity for the graphene layer, in the vicinity of which the polymerization proceeds.

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