Copolymerization of Phenanthrene and Maleic Anhydride

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SUMMARY

A study of the copolymerization of phenanthrene and maleic anhydride was carried out at 60°C using AIBN as a radical initiator. The copolymerization is characterized by the fact that these two monomers are hardly homopolymerized, and the complex formed by the two monomers may promote the copolymerization. Also, it was found that solvents having no ability to complex with monomer were good milieus for this copolymerization.

The copolymers so obtained have 1:2-1:1 composition ratios of phenanthrene and maleic anhydride.

Kinetic studies of the copolymerization were carried out under heterogeneous and homogeneous conditions in benzene and dioxane, respectively. $[\eta]$ of the copolymer in tetrahydrofuran at 30°C was found to be in the range 0.06-0.13.

The alternating copolymerization of maleic anhydride (MAH) with the usual vinyl monomers has been widely studied [1,2]. Recently such investigations have shifted toward the study of radical copolymerization with monomers which do not undergo radical homopolymerization, for example, dioxene [3] and dimethoxyethylene [4]. It has been accepted that these copolymerizations are promoted by the complex formed between two monomers or between the growing radical and MAH.

Since the character of MAH as an electron acceptor has been well known for the formation of complexes with aromatic compounds, related polymerization studies are of interest.

The authors have succeeded in copolymerizing aromatic compounds such as phenanthrene with MAH to form new copolymers.

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The rates of copolymerization and the molecular weights were influenced by the nature of solvents and are particularly sensitive to the monomer concentration. Thus it appears that concentration of complex between the two monomers strongly controlled the copolymerization.

The copolymers are formed with 1 : 1-1 : 2 (phenanthrene/MAH) composition ratios for the two monomers, and their viscosities $[\eta]$ are 0.06-0.13 in tetrahydrofuran at 30°C.

EXPERIMENTAL

Phenanthrene was purified by recrystallization from ethyl alcohol or by sublimation in vacuum. MAH was recrystallized from absolute dry chloroform. α,α'-Azobisisobutylonitrile (AIBN) was also recrystallized from ethyl alcohol. The solvents were purified by the usual method. The copolymerizations were carried out at 60°C in dry nitrogen or in a high vacuum system. The reaction mixtures were precipitated in benzene. The polymers were obtained in a powdery form, filtered, washed with benzene, and dried to constant weight in vacuum at room temperature. In the case of copolymerization for mixtures rich in maleic anhydride, the yields of copolymers were determined by precipitation in methyl alcohol in order to eliminate the small quantity of homopolymer from maleic anhydride. The viscosity measurement of polymer was carried out in THF at 30°C.

RESULTS AND DISCUSSION

Table 1 shows the influence of the nature of solvents on the polymerization rate and the molecular weights of the polymer obtained. This result indicates that solvents having the ability to undergo complex formation are not suitable. For example, no polymer was obtained in solvents having a strong electron-accepting center such as the nitrogen atom of DMF. As shown in Fig. 1, the order of the polymerizability in aromatic solvents is benzene > toluene > xylene, which is in reverse order to the strength of electron donation. It is obvious that complex formation with solvent disturbs the formation of complex between two monomers.

Dioxane and benzene were used as the solvents in the kinetic investigation, corresponding to homogeneous and hetrogeneous conditions, respectively.

It was found that the composition of the polymer obtained by polymerization in benzene and by precipitation in methyl alcohol was independent of the composition of monomers. The carbon content determined by element analysis is a little smaller than that corresponding to the 1:2 composition of phenanthrene and MAH (as shown

Table 1. Copolymerization of Phenanthrene and Maleic Anhydride in Various Solvents[a]

Solvents	Temp., °C	Yield, g	$[\eta]$	Mol. wt.	Remarks
DMF	60	0.000	—	—	Homogeneous
Dioxane	60	0.682	0.06	3600	Homogeneous
CCl$_4$	60	1.016	0.13	5800	Partly heterogeneous
CCl$_3$H	60	1.100	0.13	6100	Oily precipitant
Acetic anhydride	60	1.008	0.09	4600	Homogeneous at 60°C
Acetone	30	0.000	—	—	Homogeneous
Dichloroethane	60	1.076	0.11	—	Oily precipitant
THF	60	Trace	—	—	Homogeneous
Benzene	60	1.000	0.13	—	Heterogeneous
Toluene	60	1.011	0.07	—	Heterogeneous
Xylene	60	0.822	0.06	—	Heterogeneous

[a]AIBN = 50 mg, phenanthrene = 0.90 g, maleic anhydride = 0.50 g (1 : 1 in mol.) solvents = 5 ml, polymerization time = 48 hr in N$_2$, precipitation in MeOH. Molecular weights were determined by the ebulliometric method in acetone.
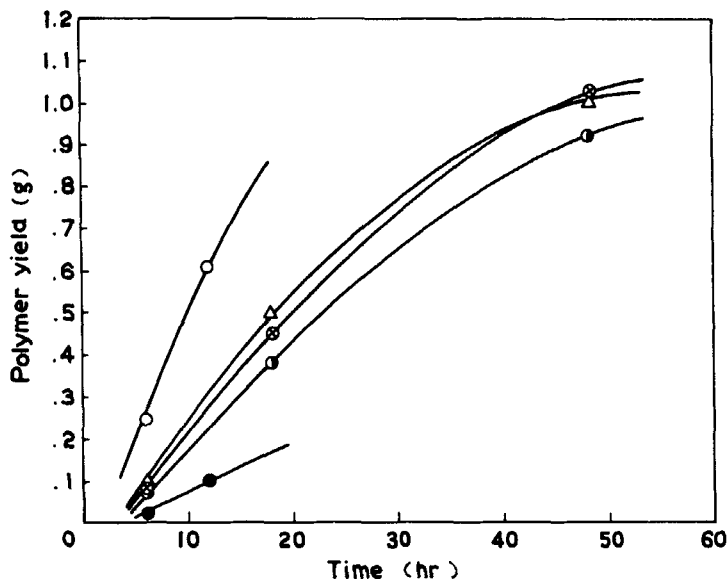
Fig. 1. Copolymerization of phenanthrene and maleic anhydride at 60°C in various solvents: ○, in benzene with 100 mg of AIBN; △, in benzene with 50 mg of AIBN; ●, in benzene with 25 mg of AIBN; ⊗, in toluene with 50 mg of AIBN; ◐, in xylene with 50 mg of AIBN. All in 0. 50 g of N_2 maleic anhydride and 0. 90 g of phenanthrene in 5 ml of solvent.

in Fig. 2). On the other hand, the results of analysis indicated that this polymer contains too much hydrogen for the 1 : 2 composition (observed 4. 3-4. 7; calculated 3. 7%). This may be explained by the esterification of minor parts of polymer at the time of precipitation in methyl alcohol, as evidenced by studies of infrared spectra. The polymer obtained by precipitation in benzene approaches the 1 : 1 composition (see Fig. 2). In the case of dioxane solution, polymer also approaches the 1 : 1 composition (as shown in Fig. 3). This phenomenon will be discussed later. The excess of hydrogen (observed: H = 4. 8; calculated: H = 4. 3% for 1 : 1 composition and 3. 7% for 1 : 2) may be caused by absorbed or reacted water and the end groups of AIBN. The IR absorption spectra of polymer also indicate the existence of the benzene ring structure (750 cm^{-1}) and the anhydride group (1860 and 1780 cm^{-1}), as shown in Fig. 4.

    The rates of copolymerization as a function of initial monomer mole ratios are given in Fig. 5. In the case of dioxane solution, the maximum rate of polymerization is achieved where MAH is in
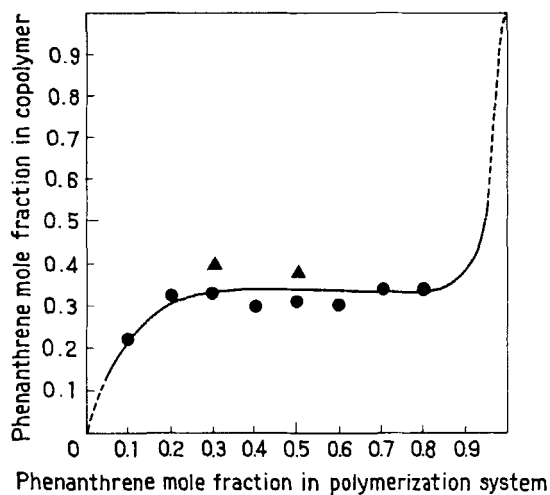
Fig. 2. Phenanthrene mole ratio in copolymer obtained in benzene solution at 60°C. ●, Precipitated in methyl alcohol; ▲, precipitated in benzene.
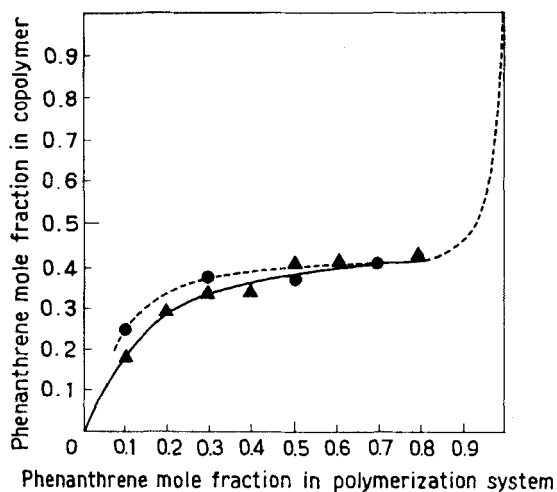

Fig. 3. Phenanthrene mole fraction in copolymer obtained in dioxane solution at 60°C. ●, Precipitated in methyl alcohol; ▲, pre-cipitated in benzene.

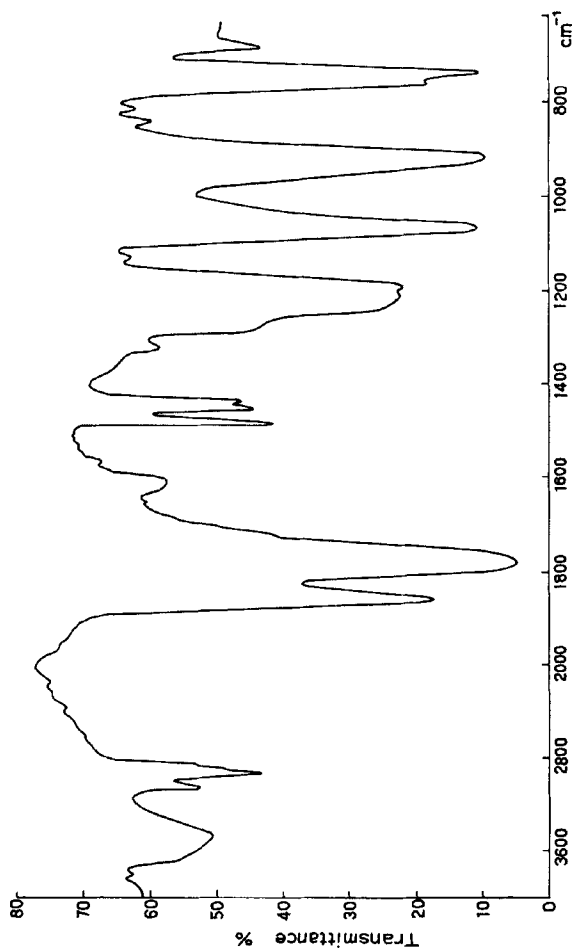*Yasuharu Nakayama, Koichiro Hayashi, and Seizo Okamura*

Fig. 4. Infrared spectrum of copolymer of maleic anhydride and phenanthrene obtained by radical polymerization in benzene at 60°C. Polymerization time, 20 hr; concentration of each monomer, 1.0 mole/liter; concentration of AIBN, 0.12 mole/liter; KBr disk method.
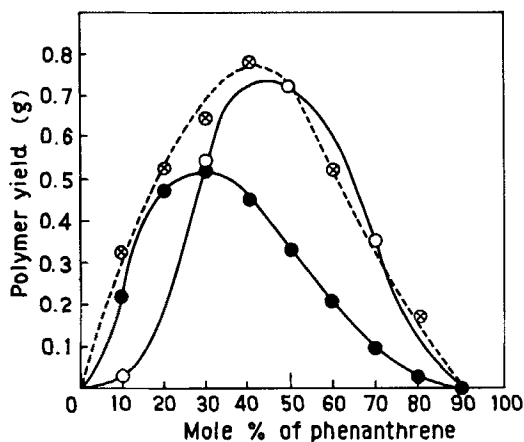
Fig. 5. Copolymerization of phenanthrene and maleic anhydride. Effect of the monomer composition. ●, 100 mg of AIBN in 5.0 ml of benzene solution for 6.5 hr. Precipitation in MeOH. ○, 100 mg of AIBN in 5.0 ml of dioxane solution for 24 hr. Precipitation in MeOH. ⊗, 100 mg of AIBN in 5.0 ml of dioxane solution for 24 hr. Precipitation in benzene. Total concentration of monomers, 2.0 moles/liter.

slight excess; however, in the case of polymerization in benzene, this maximum rate appeared at the 1 : 2 mole composition of phenanthrene and MAH, respectively. Considering this result in comparison with the polymer composition, a very interesting relation is found. It is possible to write three propagating reactions, as follows:

(1)

1:2 copolymer

(2)

1:1 copolymer

(3)

1:2 copolymer
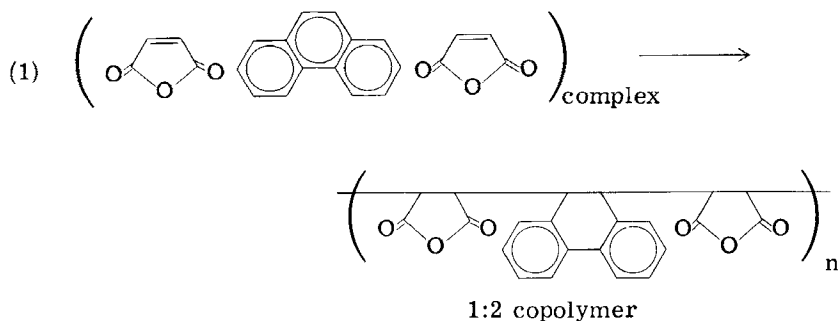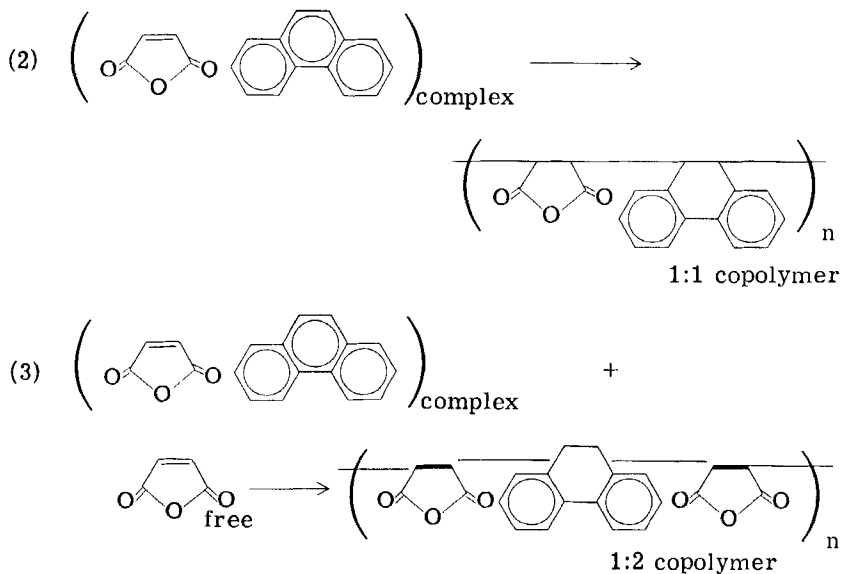
The experimental results suggest that routes 1 or 3 are predominant. But when the UV absorption spectrum of the complex was measured at a fixed total concentration of the two monomers, the maximum point appeared approximatively at the 1 : 1 composition of the two monomers. This indicates the existence of a 1 : 1 complex and the probability of route 3. The polymerization at a fixed concentration of one monomer and a variable concentration of the other monomer was examined. The results are shown in Figs. 6 and 7. A large excess of phenanthrene decreases the rate of polymerization, and this is caused by the character of phenanthrene rather than the impurity contained in phenanthrene, because no difference was observed in using phenanthrene purified by two different methods, sublimation and recrystallization. This result can be explained by the difficulty of process 3 because of the decreasing concentration of free maleic anhydride. The polymer yields as a function of polymerization time for various compositions of the two monomers are summarized in Fig. 8. Some induction periods are observed in all cases, particularly in the case of high concentrations of phenanthrene. This phenomenon was also observed for the polymerization in the homogeneous system.

The maleic anhydride radical with a positive charge at the attacking site hardly attacks maleic anhydride monomer, which also bears a positive charged at the $C=C$ double bond; however, it may be possible for the radical to react with the monomer in the state of π
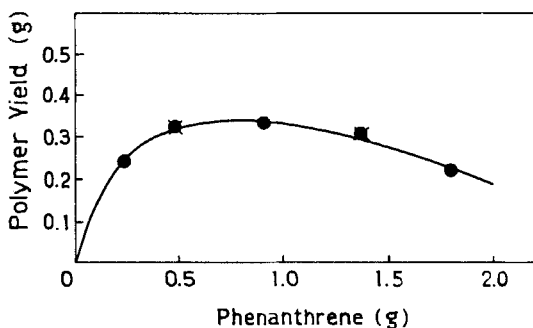
Fig. 6. Copolymerization of phenanthrene and maleic anhydride.
The effect of the amount of phenanthrene. Maleic anhydride, 0. 50 g;
AIBN, 100 mg; time of polymerization, 6. 5 hr; solvent, benzene;
temperature, 60°C in N_2, total volume, 5. 0 ml. ×, phenanthrene puri-
fied by sublimation in vacuo, ●, phenanthrene purified by recrystali-
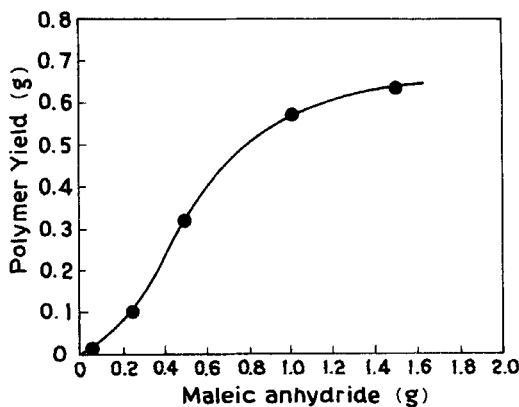zation from ethyl alcohol.

Fig. 7. Copolymerization of phenanthrene and maleic anhydride.
The effect of the amount of maleic anhydride. Phenanthrene, 0. 45 g;
AIBN, 100 mg; time of polymerization, 6. 5 hr; solvent, benzene;
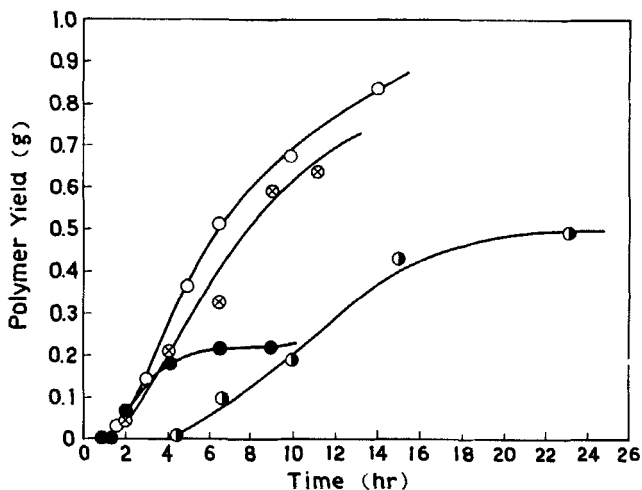temperature, 60°C in N_2; total volume, 5. 0 ml.

Fig. 8. Copolymerization of phenanthrene and maleic anhydride. 100 mg of AIBN in benzene solution at 60°C. ●, 0.18 g of phenanthrene, 0.90 g of maleic anhydride; ○, 0.54 g of phenanthrene, 0.70 g of maleic anhydride; ⊗, 0.90 g of phenanthrene, 0.50 g of maleic anhydride; ◐, 1.26 g of phenanthrene, 0.30 g of maleic anhydride. Total volume, 5.0 ml.

complex with phenanthrene, because this monomer is then relieved from the positive charge as follows:
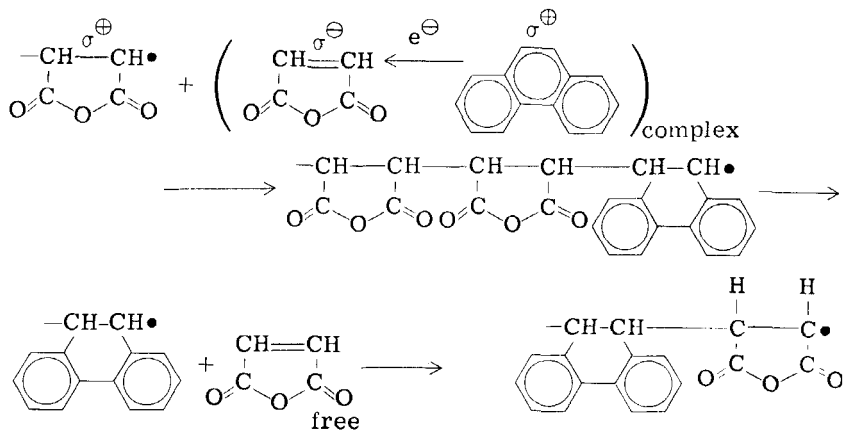
Phenanthrene radical easily reacts with free MAH and gives the co-polymer formed according to the 1 : 2 composition (phenanthrene/MAH). Considering the termination reaction, the cross termination

might be more favorable, and this contributes to an increase in the phenanthrene content above 1 : 2 (phenanthrene/MAH) in copolymer composition.

After that, the composition of copolymer is considered as follows:

n and m = 0, 1, 2, ...
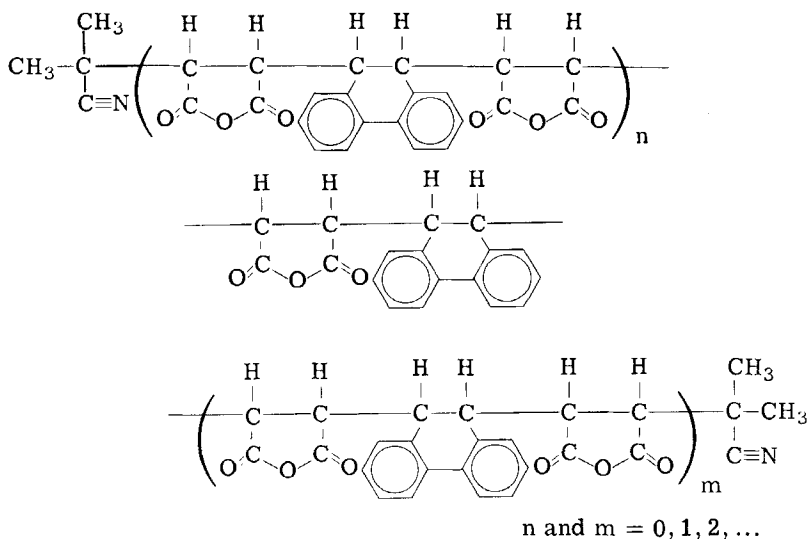
The polymer obtained by precipitation in benzene or by polymerization in dioxane contains a large amount of low molecular weight copolymer. This indicates the approach to 1 : 1 composition. On the other hand, the high molecular weight polymer obtained by polymerization in benzene and precipitated in methanol shows the 1 : 2 composition. The copolymer obtained in dioxane solvent has a low molecular weight and the rate of polymerization in this solvent is slower than in benzene, which may be explained by the low concentration of complex and the possibility of the formation of δ-type propagating radical-dioxane complex.

In the case of the homogeneous system, Fig. 9 shows that the order of the polymerization rate is approximately 0.5 in relation to the initiator concentration. But as shown in Fig. 10, a large decrease of polymerization rate was observed as the concentration of monomer was reduced. This is explained by the assumption that only the complex can be polymerized, because the formation of the complex represents a competition between monomer-monomer and monomer-solvent interaction, and it is observed that the concentration of monomer largely influences the concentration of complex. In fact, as shown in Fig. 11, the UV absorption spectra of this polymerization solution show a large diminution of complex absorption intensity ($>$ 390 mμ) with decreasing concentration of monomer.
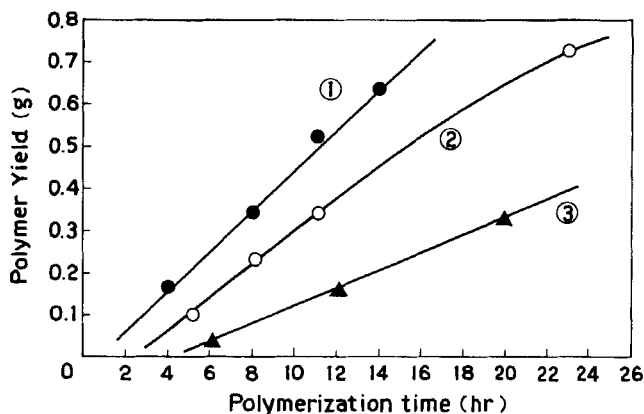
Fig. 9. Copolymerization of phenanthrene and maleic anhydride. Phenanthrene, 0.90 g; maleic anhydride, 0.50 g; in dioxane solution. ①, 200 mg of AIBN; ②, 100 mg of AIBN; ③, 50 mg of AIBN. Total volume, 5.0 ml in N_2 at 60°C.
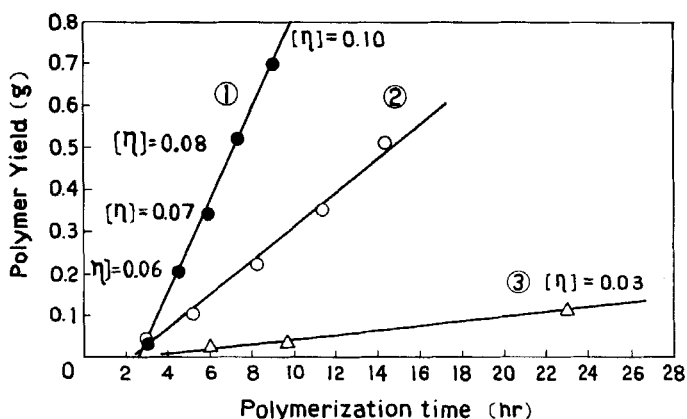

Fig. 10. Copolymerization of phenanthrene and maleic anhydride. 100 mg of AIBN in dioxane solution; total volume, 5.00 ml. ①, 1.8 g of phenanthrene, 1.0 g of maleic anhydride; ②, 0.9 g of phenanthrene, 0.50 g of maleic anhydride; ③, 0.45 g of phenanthrene, 0.25 g of maleic anhydride.
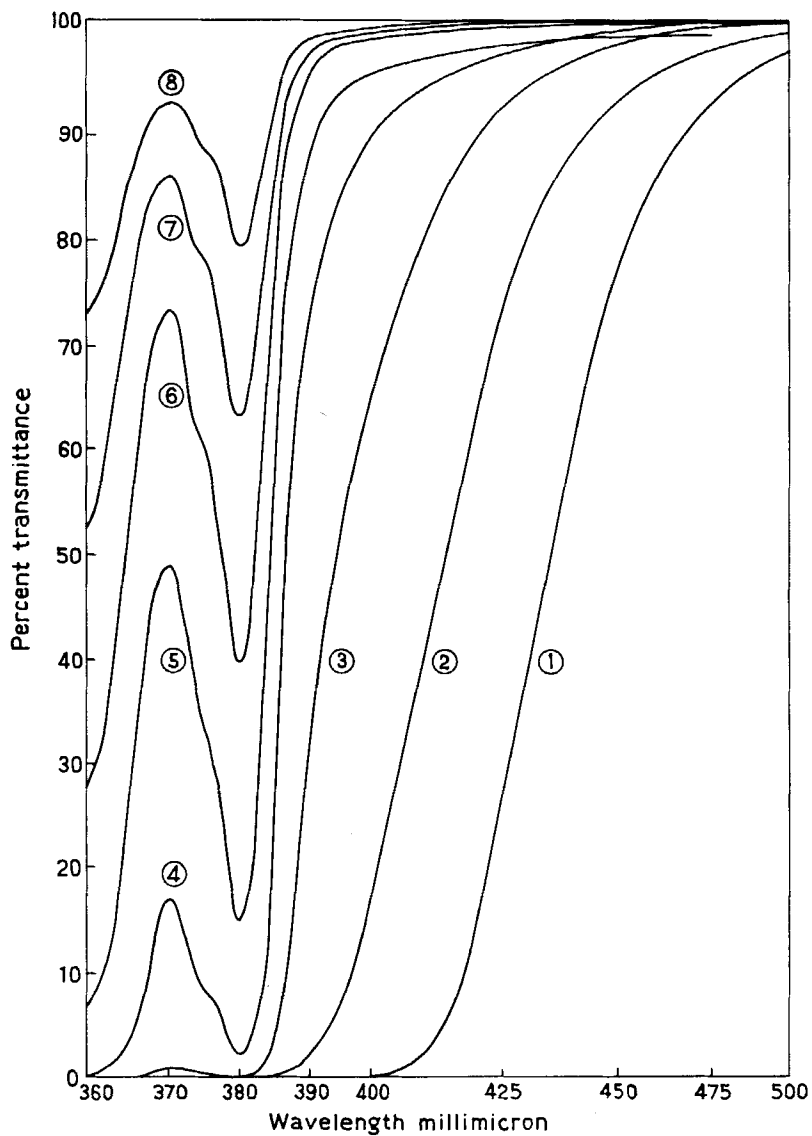
Fig. 11. UV absorption spectra of the complex of phenanthrene and maleic anhydride. Concentrations of each monomer in benzene. ①, 0.51 mole/liter; ②, 0.26; ③, 0.13; ④, 0.065; ⑤, 0.033; ⑥, 0.017; ⑦, 0.008; ⑧, 0.004.

As indicated in Fig. 10, the viscosity of the polymer obtained increases with the polymerization time. This phenomenon can be explained by the assumption of a very small propagation rate. It is also possible to explain the long induction period (Fig. 8) by means of this assumption, since a certain time would be necessary to form polymer which has a large molecular weight and can be precipitated.

The possibility of the polymerization resulting from an ionic addition reaction between the two monomers is denied by the following facts. First, before polymerization, the system was heated for a long time (7 hr) in the absence of AIBN, but the polymer yield was not changed. Second, the reaction between the phenyl group in the copolymer and MAH is also not probable, because when diphenyl was used instead of phenanthrene, the diphenyl was completely recovered after heating with MAH.

An attempt was made to initiate the copolymerization with UV irradiation, and after 10 hr 0.58 g of polymer was formed from the mixture of 0.54 g of phenanthrene and 0.70 g of maleic anhydride in 2 cc of benzene. But the product had a very low molecular weight ($[\eta] = 0.03$). In this case, biradicals produced by UV light react with phenanthrene or maleic anhydride to form the cyclic dimer [5] because of the low propagating rate.

Gamma irradiation also gives a low molecular weight polymer. In this case, the decomposition of polymer is not negligible in comparison with the propagating rate.

Several experiments were carried out with a variety of donors. Pyridine reacts with MAH as an organic base. Naphthalene and chrysene gave no copolymer, and pyrene produced a low molecular weight white powder at 100°C.

In conclusion, it is very impressive that an aromatic hydrocarbon such as phenanthrene was copolymerized with MAH, and that the copolymer so obtained had a dominant composition of MAH.

ACKNOWLEDGMENT

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