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The Preparation and Properties of the Condensed Polynuclear Aromatic (COPNA) Resins Using an Aromatic Aldehyde as Crosslinking Agent(1)

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Thermosetting resins composed of triarylmethane structure were prepared by heating a mixture of a polycyclic aromatic compound and an aromatic aldehyde in the presence of an acid catalyst. The resin prepared from the mixture of pyrene and terephthalaldehyde exhibited scarcely any weight loss up to 530 °C under nitrogen. While the resin from anthracene has such high carbon yield as 70% at 800 °C, although its thermostability is somewhat inferior.

In a previous paper,(2) the present authors have reported on COPNA resins prepared from polycyclic aromatic compounds(Aro) and 1,4-benzenedimethanol(PXG). The COPNA resins composed of aromatic nuclei crosslinked with p-xylylene bond exhibited extremely high thermostability.(3-5) This results prompted us to study the preparation of a new COPNA resin with a different type of new linkage form other than the xylylene bond. After some trials, the new resins crosslinked with methine bond were sucessfully prepared using such aromatic aldehydes as benzaldehyde(BA), and terephthalaldehyde(TPA) as crosslinking agent.

The composition of raw mixtures and the reaction conditions are summarized in Table 1. The raw mixture containing aromatic compound(Aro), TPA and PTS melted to become a clear liquid by heating under an argon stream and was finally converted to an infusible and insoluble solid via a highly viscous state by further heating. This highly viscous product at the reaction temperature is called as a "B stage resin". The B stage resin solidifies after cooling to room temperature and is soluble and fusible. As shown in Table 1, pyrene(Py) was more reactive than anthracene. The B stage resin from pyrene was lustrous dark green and the resin from anthracene was lustrous black. The similar resins to them were also prepared using BA as the crosslinking agent. The structure of the product at each reaction step until B stage resin was analysed by IR and NMR spectroscopy. The thermostability of the resin after post-curing at 300 °C for 1 h was evaluated by thermogravimetric analysis(TGA).

Table 1. The composition of raw mixture, the preparation conditions and softening point of the obtained B stage resins

Aro	TPA/Aro[a)]	PTS[b)] wt%	Reaction temp/°C	Reaction time/h	Yield %	Softening point/°C
Pyrene	1.5	5	160	1.5	94	80
Anthracene	1.5	5	200	4.5	90	80

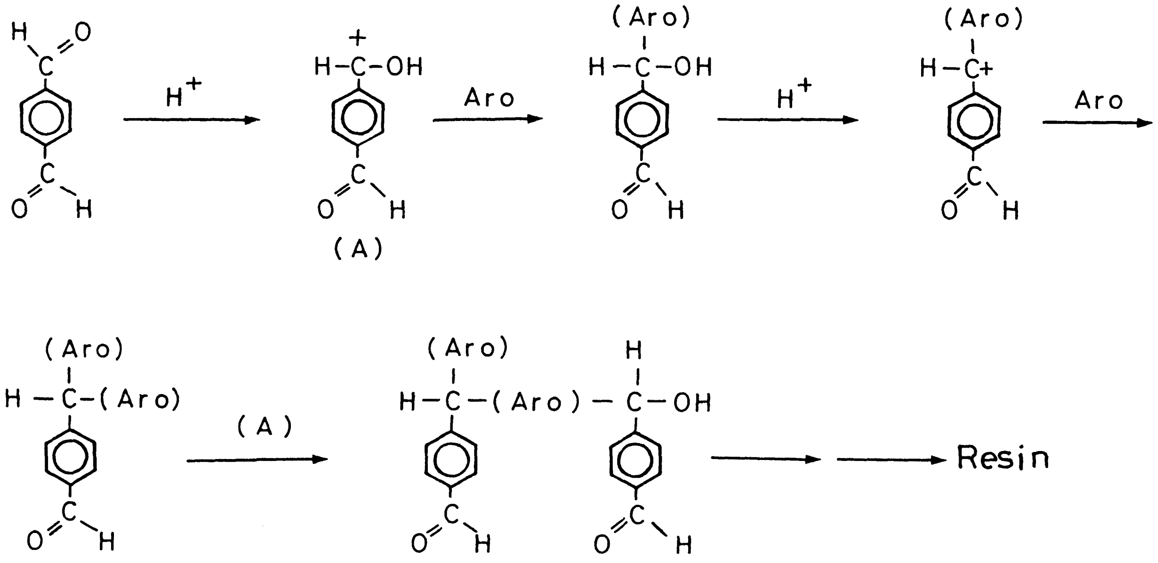
a) TPA/Aro shows the molar ratio of TPA to Aro in the mixture.
b) Acid catalyst : p-toluenesulfonic acid.

In the case of the TPA/Py based resin, an absorption at 1700 cm^{-1} which was assigned to an aldehyde group weakened and absorptions around 1180 cm^{-1} and 1600 cm^{-1} appeared. The absorption band at 1180 cm^{-1} may be assigned to hydroxyl groups which produced in the course of reaction and another one at 1600 cm^{-1} can be assigned to carbonyl groups which are hydrogen-bonded to the above hydroxyl group. As the reaction proceeds, the absorption due to three neighboring hydrogens at 1, 2, and 3 positions in pyrene around 750 cm^{-1} weakened slightly. The absorptions at 1700 cm^{-1}, 1600 cm^{-1}, and 1180 cm^{-1} also decreased, but did not disappear even after post-curing.

From the results of the C-H correlation spectroscopy(COSY) based on ^{13}C and ^{1}H NMR spectra of the B stage resin, it was found that the peak around 50 ppm in ^{13}C NMR spectra assigning to methine carbon appeared and its intensity increased with decrease of the peak intensity of aldehyde-type carbon.

The substituted positions in pyrene nucleus were not determined exactly, but it is most probable that substitution occurs at the two positions among 1, 3, 6, and 8. On the basis of the results stated above, it may be reasonable to consider that this new type of the COPNA resin is formed through a crosslinking reaction caused by aldehyde group as shown in the following equation.

At the first step of reaction, the carbocation derived from the aldehyde group of TPA should electrophilically attack pyrene and then the carbocation produced from hydroxyl group formed at the first step should attack another pyrene. This assumption is supported by the fact that the similar resin is prepared even by using a mono-substituted compound like benzaldehyde(BA).



The structural model of the resin finally obtained is shown in Fig. 1. The essential feature of this model is characterized by the triarylmethane structure, although some amounts of unreactive aldehyde and hydroxyl groups remain.

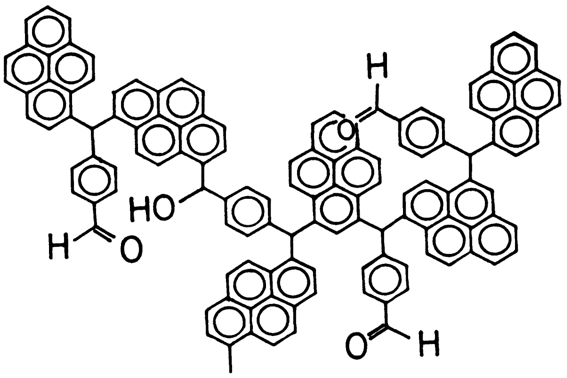


Fig. 1. The triarylmethyl structure of COPNA resin.

Therefore, this new type of COPNA resin can be called a "triarylmethane resin".

Figure 2 shows TGA curves for the two resins prepared by post-curing at 300 °C. The weight of TPA/Py based resin decreased suddenly by 25% at 530 °C. The carbon yield at 800 °C was 51 wt%. In view of the thermostability and the carbon yield, the TPA/Py based resin is superior to the PXG/Py based resin reported previously.3) As shown in Fig. 2, the weight loss of the TPA/anthracene-based resin initiated at a lower temperature than that of the TPA/Py based resin. The carbon yield of 70 wt% at 800 °C, however, was remarkably larger than that of the TPA/Py based resin.

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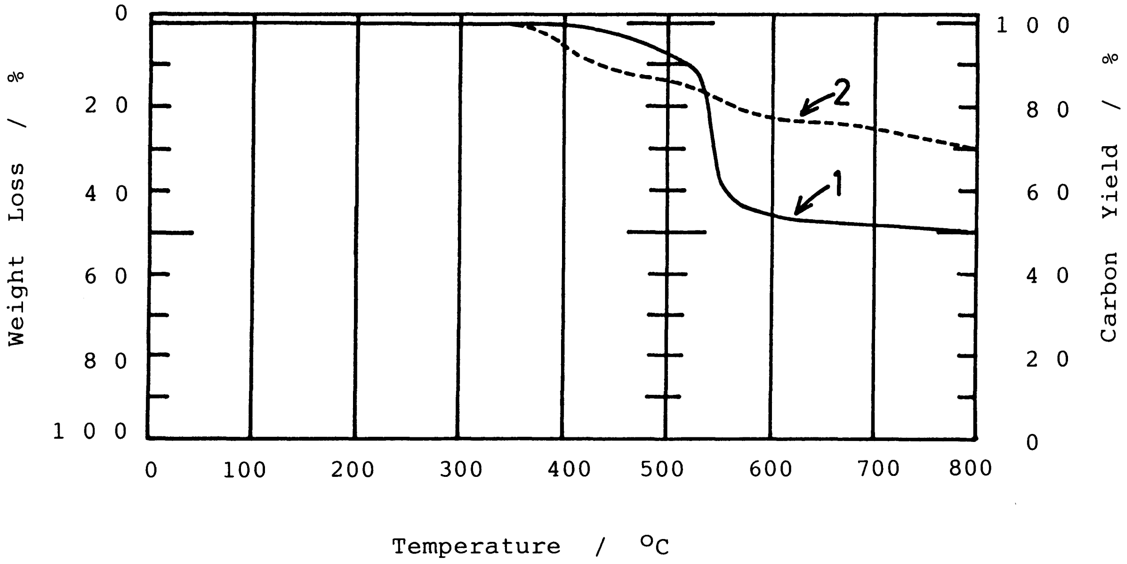

Fig. 2. Weight loss of the resins post-cured at 300 °C for 1 h. (heating rate : 10 °C/min under nitrogen)
1 : TPA/Py based COPNA resin, 2 : TPA/Anthracene based COPNA resin

References

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