

LETTERS TO THE EDITOR

PREPARATION OF AROMATIC POLYAMIDES BASED ON PHENYLENE DIAMINES

CONSIDERABLE attention has been drawn on the preparation and characterization of polyamides from aliphatic diamines with aromatic diacids. Although the wholly aromatic parapolyamides and isopolyamides have received considerable importance as high temperature fibres, no detailed reports are available on the effect of different parameters on polymerization reactions¹⁻⁶. A detailed survey on the preparation, characterization and utilization of aromatic polyamides for fibres was reviewed recently⁷. Various reports are available on the use of sulphuric acid as the polymer solvent for making fibres. A few recent reports give an account of the addition of LiCl or CaCl₂ to organic solvents such as DMAC, DMF, THF, etc., to get transparent spinning dopes⁸⁻¹¹. In this paper we have attempted to study the interfacial and solution polymerization of wholly aromatic polyamides in the presence of LiOH as catalyst, which initially performs the catalytic role and subsequently improves the solubility as the corresponding chloride salt.

Experimental

Materials

The phenylenediamines (AR, BDH) were purified by vacuum sublimation through coarse filter paper. The purified diamines remained white and undegraded when stored in brown bottles in a nitrogen atmosphere. Diacid chlorides (AR, BDH) were purified as follows: Isophthaloylchloride was crystallised from dry hexane, 42-44° C. Terephthaloylchloride was crystallised from boiling petroleum ether 40-60° C, m.p. 83-85° C.

Methods of polymer preparation

Solution polymerization: Various molar ratios of meta or para diamines (0.02 M to 0.15 M) (I) and iso- or terephthaloylchlorides (0.05 M to 0.15 M) (II) were taken separately in 100 ml solvent (DMF or DMAC or THF or dichloromethane). The acid acceptor (LiOH) (twice the diamine concentration) was added to (I). I and II were cooled to 0-5° C. The cooled solution II was added dropwise to the cooled solution I with stirring in 10 minutes and the reaction was continued for another 30 minutes. The solution as such could be employed for spinning. A portion of the solution was precipitated with water and the polymer was filtered, washed with 5% aqueous hydrochloric acid, acetone-water (1:1 V/V) and finally with water. The viscosity of the polymer was determined in 96% sulphuric acid.

Interfacial polymerization

A solution of meta or para phenylenediamine (0.02 M to 0.15 M) and the catalyst (twice that of diamine concentration) was taken in 235 ml of water (I). Iso- or terephthaloyl chloride was taken in 65 ml of cyclohexanone (II). The reaction was carried out as per the details given above by solution polymerization.

Viscosity measurements

The inherent viscosities of all polymers were measured at 30° C using 0.5 g of polymer in 100 ml of 96% concentrated sulphuric acid using the relationship

$$\eta_{inh} = 2.303 \frac{\eta_{rel}}{C} \text{ dl/gm.}$$

Results and Discussion

Effect of catalyst concentration

The catalyst concentrations on the rate of solution polymerization was studied by varying the concentration from 0.02 M to 0.12 M keeping meta or para diamine and Iso- or terephthaloylchloride at 0.05 M. It was found from Fig. 1 that at least two moles of acid acceptor are required per mole of diamine in order to get the maximum yield and high molecular weight polymer. Further if the ratio of the catalyst was more than twice that of diamine concentration, it was found that there was both decrease in the yield as well as the molecular weight of the polymer.

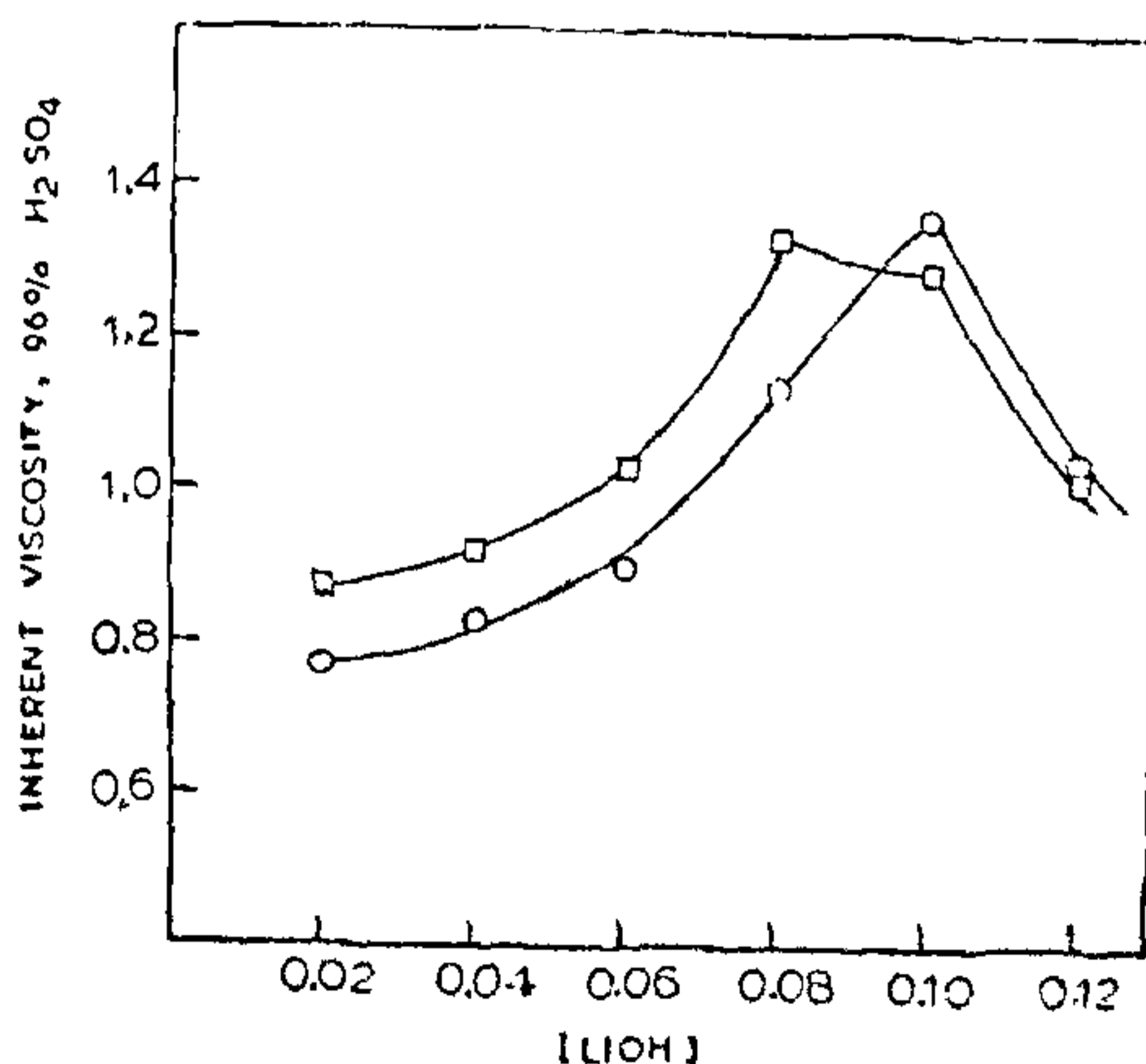


Fig. 1. Effect of catalyst conc.

○ *m*-phenylenediamine/Isophthaloylchloride (0.05 M);
 □ *p*-phenylenediamine/Terephthaloylchloride (0.05 M).

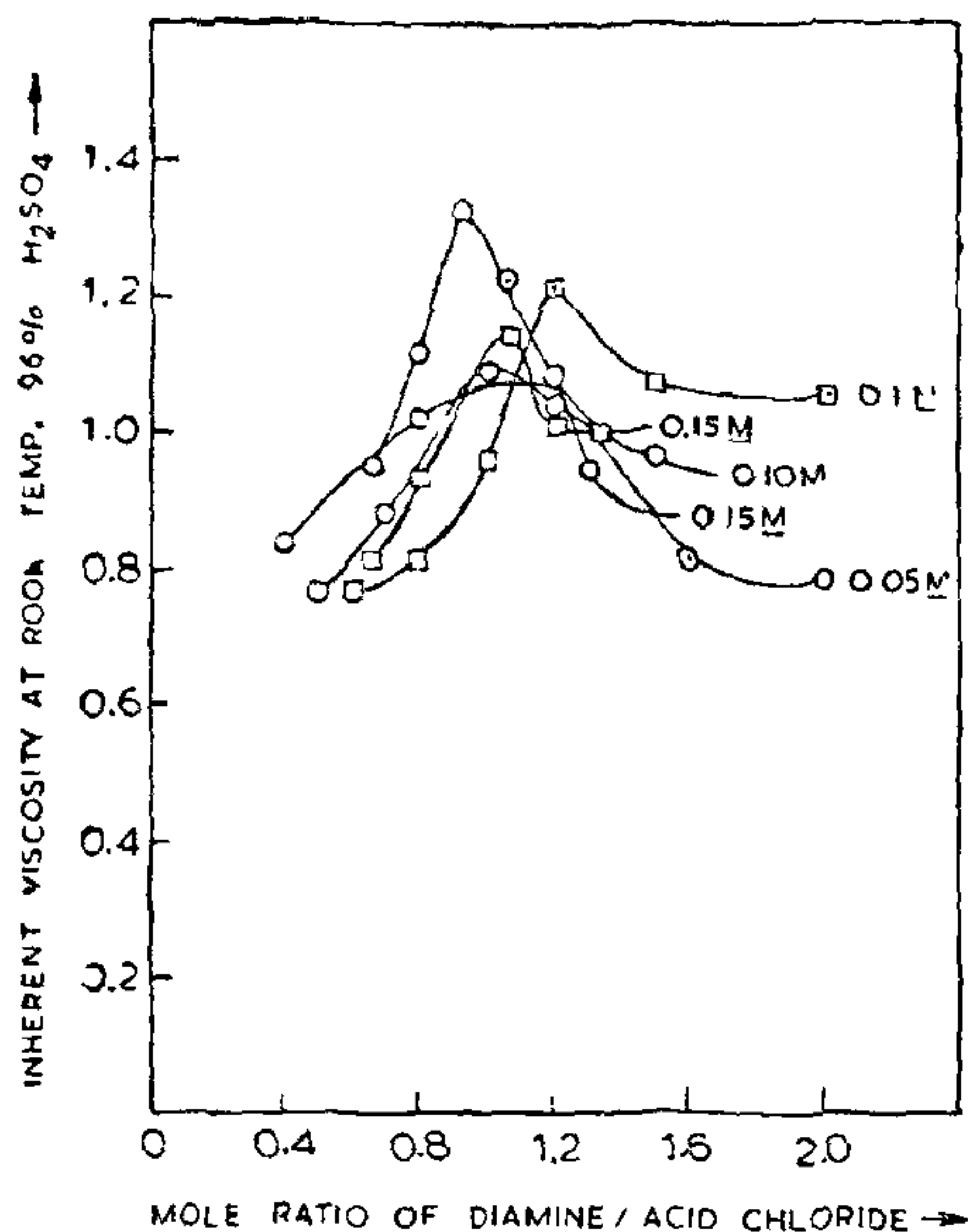


FIG. 2. Effect of mole ratios.

○ *m*-phenylenediamine/Isophthaloylchloride;
 □ *p*-phenylenediamine/Terephthaloylchloride.

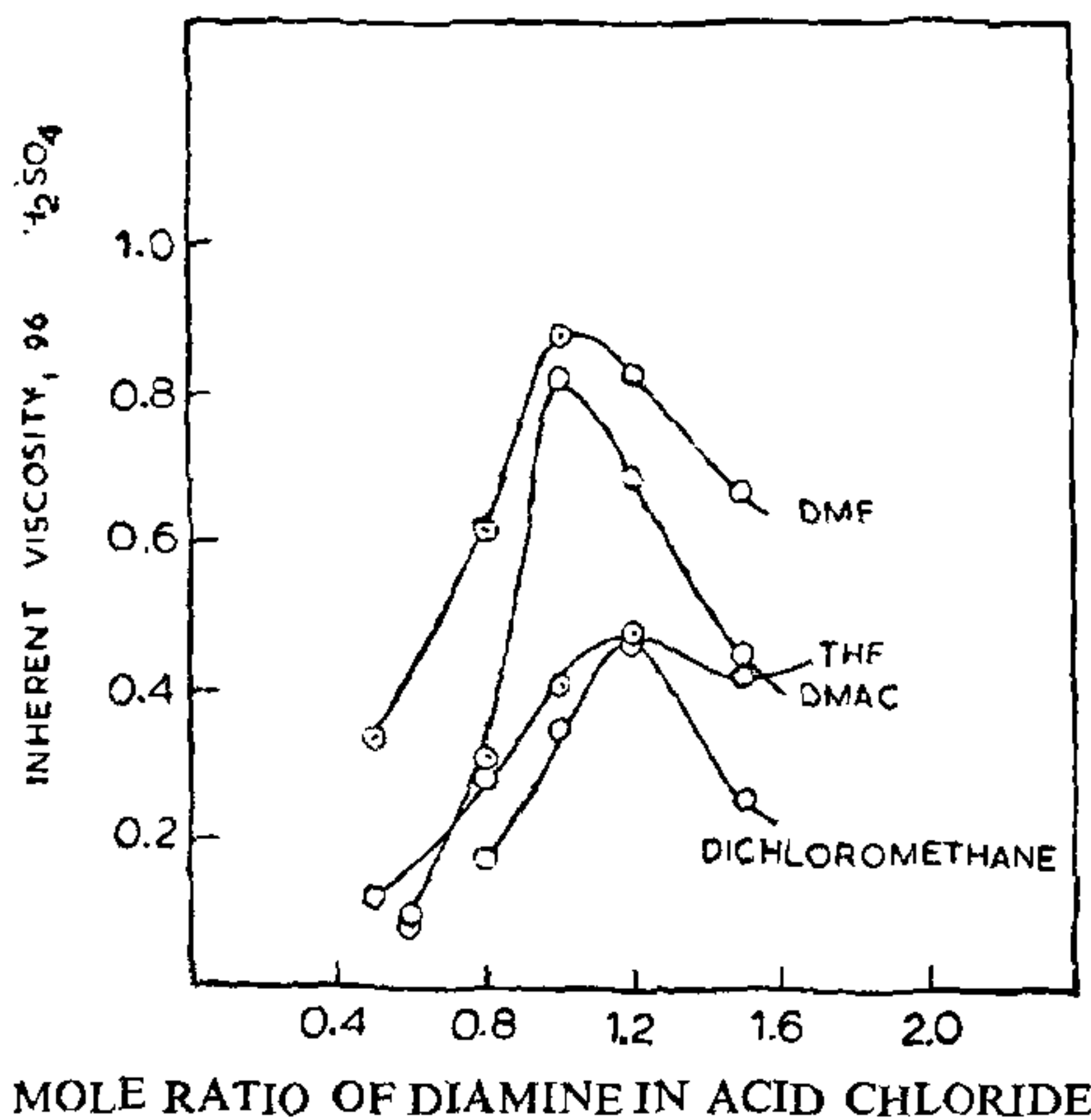


FIG. 3. Effect of solvents.

Effect of temperature

The polymerization reactions were conducted at three different temperatures (0°C , 5°C and at 30°C). It was noticed that the yield and also the viscosity of

the polymer was more when the reaction was carried out at 0°C .

Effect of molar ratios of reactants

Diacid chloride concentration was kept constant (0.05 M or 0.10 M) and the concentration of meta or para phenylenediamine was varied from 0.02 M to 0.15 M (Fig. 2). It was found that the best molar ratio of meta or para phenylenediamine to iso- or terephthaloylchloride was 1.0 to 1.25 M.

Effect of solvents

The rate of polymerization was studied using different solvents such as dimethylformamide, dimethylacetamide, tetrahydrofuran and dichloromethane (Fig. 3). It was found that the yield as well as the viscosity of the polymer followed the order $\text{DMF} > \text{DMAc} > \text{THF} > \text{Dichloromethane}$. In general it is observed that the solution polycondensation produces higher molecular weight polymers.

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