Existence of a penultimate effect in the cationic copolymerization of 1-isopropenyl naphthalene with styrene

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INTRODUCTION

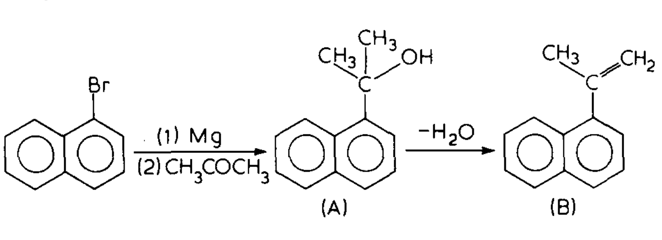
The homopolymerization of 1-isopropenyl naphthalene gives a cyclic dimer only, whatever the experimental conditions[1,2]. The structure of the dimer has been described previously[1]. Such behaviour is analogous to that of 3-methyl indene whose cationic polymerization and copolymerization have been studied by Sigwalt and Maréchal[3].

By determining the reactivity ratios of the system 3-methyl indene–styrene these authors have shown the existence of a marked penultimate effect[3]. In the present work a similar study is carried out for the system 1-isopropenyl naphthalene styrene.

EXPERIMENTAL

1-isopropenyl naphthalene

This has been prepared according to the following scheme:



1-(1-naphthyl) 1-methyl ethanol. (A) 1 mol of magnesium (24.3 g), a crystal of iodine and 100 CC of ethyl oxide are placed in a 2 litre flask, fitted with a stirrer, a reflux condenser and a dropping funnel. A solution of 1 mol (207 g) of 1-bromo naphthalene in 500 CC of sodium dried ether is added over 2 h. At the end of the introduction ether is refluxed for 30 min after which 1 mol (58 g) of propanone in 250 CC of sodium dried ether is dropped into the Grignard reactant. The mixture is then cooled and poured into an aqueous solution of ammonium chloride. The organic layer is separated and ether is distilled off. A precipitates and is crystallized in light petroleum ether. (*Y*%: 80; M.P. °C: 85; Analysis $C_{13}H_{14}O$ Calculated: C 83.87; H 7.53 Determined: C 83.8; H 7.5).

1-isopropenyl naphthalene. (B) 10 g of A and 2 g of potassium hydrogenosulphate are placed in a Claisen flask and heated in vacuum, B distils. (Y%: 30; Eb_{10} 130°C; Analysis $C_{13}H_{12}$ Calculated: C 92.86; H 7.14 Determined C 92.8; H 7.2).

Methylene chloride

Methylene chloride is refluxed in 20% oleum with stirring for 24 h. After elimination of the acidic phase, the methylene chloride is washed twice in water, then twice in a sodic solution and again five times in water. The resulting solvent is distilled through an efficient column; the purity is controlled by gas chromatography.

Titanium tetrachloride

Titanium tetrachloride is purified by distillation through an efficient column.

RESULTS AND DISCUSSION

Since only two monomer units of 1-isopropenyl naphthalene can be associated, due to steric hindrance, it is necessary to calculate the reactivity ratios relative to the system 1-isopropenyl naphthalene–styrene using the following set of equations[4]:

$$\begin{array}{lcl}
\sim M_1M_1^{\oplus} + M_1 & \xrightarrow{k_{111}} & \sim M_1M_1M_1^{\oplus} \\
\sim M_1M_1^{\oplus} + M_2 & \xrightarrow{k_{112}} & \sim M_1M_1M_2^{\oplus} \\
\sim M_1M_2^{\oplus} + M_1 & \xrightarrow{k_{121}} & \sim M_1M_2M_1^{\oplus} \\
\sim M_1M_2^{\oplus} + M_2 & \xrightarrow{k_{122}} & \sim M_1M_2M_2^{\oplus} \\
\sim M_2M_1^{\oplus} + M_1 & \xrightarrow{k_{211}} & \sim M_2M_1M_1^{\oplus} \\
\sim M_2M_1^{\oplus} + M_2 & \xrightarrow{k_{212}} & \sim M_2M_1M_2^{\oplus} \\
\sim M_2M_2^{\oplus} + M_1 & \xrightarrow{k_{221}} & \sim M_2M_2M_1^{\oplus} \\
\sim M_2M_2^{\oplus} + M_2 & \xrightarrow{k_{222}} & \sim M_2M_2M_2^{\oplus}
\end{array}$$

which leads to equation 1:

$$y=\frac{1+\dfrac{r'_1x(r_1x+1)}{r'_1x+1}}{1+\dfrac{r'_2}{x}\left[\dfrac{r_2+x}{r'_2+x}\right]} \qquad (1)$$

where $x=\dfrac{M_1}{M_2}$, $y=\dfrac{m_1}{m_2}$; m_1, m_2, M_1, M_2 being the molar fractions of monomers M_1 and M_2 in the copolymer and the feed respectively. This treatment gives rise to four reactivity ratios:

$$r_1=\frac{k_{111}}{k_{112}};\ r'_1=\frac{k_{211}}{k_{212}};\ r_2=\frac{k_{222}}{k_{221}};\ r'_2=\frac{k_{122}}{k_{121}}$$

Since 1-isopropenyl naphthalene does not polymerize above dimer: $r_1=0$; we can assume that no penultimate effect takes place in the polymerization of styrene which gives $r_2=r'_2$. Thus equation 1 simplifies to:

$$r'_2=x(y-1)+x^2y\frac{r'_1}{r'_1x+1} \qquad (2)$$

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Experimental results and relative equations are reported in *Table 1*.

The corresponding hyperboles are plotted in *Figure 1*, the corresponding values of reactivity ratios are: $r'_1=0.4$ and $r'=2.35$.

Since $r'_2=r_2$ is above 1, 1-isopropenyl naphthalene is less reactive then styrene. This corresponds to the fact that, due to the steric interference between the isopropenyl group and hydrogen in position 8, the isopropenyl group is shifted out of the plane of the naphthyl ring. This results in a decrease in the conjugation between the double bond and the ring.

^{1}H n.m.r. spectra of the copolymers shows that no cyclic dimer[1] is obtained which means that the rate of copolymerization is far above the rate of termination by cyclization. This proves that the fact that 1-isopropenyl naphthalene gives only a dimer is due to steric hindrance.

As a comparison we determined reactivity ratios by Kelen and Tudos[5,6] which does not take the penultimate effect into consideration. The values obtained are the following:

$$R_1=\frac{k_{11}}{k_{12}}=0.2 \quad , \quad R_2=\frac{k_{22}}{k_{21}}=2.3$$

It can be observed that $R_2=r'_2$ which is reasonable since there is no penultimate effect in styrene polymerization. Moreover R_1 is between 0 (r_1) and 0.4 (r'_1) which corresponds to the fact that sequence above two units cannot be obtained.

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Table 1 Copolymerization of 1-isopropenyl naphthalene (M_1) with styrene (M_2) in methylene chloride. $[M_1]+[M_2]=0.1$ mol. l^{-1}; $[TiCl_4]=0.002$ mol. l^{-1}. Temperature (°C) = −75

$[M_1]$	$[M_2]$	m_1	m_2	$r'_2=f(r'_1)$
0.02	0.08	0.093	0.907	$r'_2=2.18+\frac{0.6\,r'_1}{0.25r'_1+1}$
0.03	0.07	0.152	0.848	$r'_2=1.97+\frac{1.03\,r'_1}{0.43r'_1+1}$
0.04	0.06	0.207	0.793	$r'_2=1.89+\frac{1.74\,r'_1}{0.67r'_1+1}$
0.05	0.05	0.268	0.732	$r'_2=1.73+\frac{2.73\,r'_1}{r'_1+1}$
0.06	0.04	0.353	0.647	$r'_2=1.25+\frac{4.12\,r'_1}{1.5r'_1+1}$

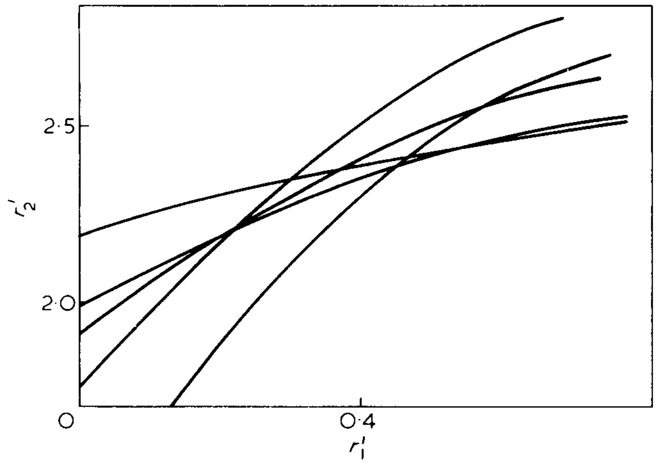

Figure 1 Copolymerization of 1-isopropenyl naphthalene (M_1) with styrene (M_2) in methylene chloride. $[M_1]+[M_2]=0.1$ mol. l^{-1}; $[TiCl_4]=0.002$ mol. l^{-1}; temperature (°C) = −75

Synthesis of poly-*p*-phenylene sulphide by oxidation of thiophenol with thionyl chloride in the presence of aluminium chloride

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INTRODUCTION

The utility of the Friedel–Crafts reaction as a method for the synthesis of network polymers was drawn to attention by Phillips[1] but it was only recently that Lewis acids were applied in the synthesis of polyarylene sulphide polymers[2,3]. Polyarylene sulphides have had wide application[4] and several methods for the synthesis of the polymers are based on pressure processes[5,6].

In the present work a new method for the synthesis of poly-*p*-phenylene sulphide by oxidation of thiophenol with thionyl chloride in the presence of aluminium chloride in benzene is described. An insoluble polymer, melting at 210–215°C was isolated.

EXPERIMENTAL

Thionyl chloride (0.1 M) was added dropwise to a solution of thiophenol (0.1 M) and aluminium chloride (0.01 M) in benzene. The reaction mixture was then heated at boiling temperature for 12 h and then poured into dilute sulphuric acid. The precipitate was filtered off, washed with

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