Phenolic resins for for oil varnishes: 1. One-step process for the preparation of a p-tert-butylphenol novolac

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A novolac was prepared from: *p*-tert-butylphenol (pure grade): 1 mol, paraformaldehyde (92% formaldehyde): 0.8 mol as formaldehyde, oxalic acid (pure grade): 0.02 mol, total water: 1.1 mol. The water content is close to 50% of the amount which would be present if the formaldehyde source were the aqueous commercial solution, 37% wt/wt. We have shown this amount to be efficient in the preparation of novolacs from paraformaldehyde[1].

The reactor was a one litre stainless steel vessel provided with an anchor impeller and a jacket for circulating oil from a thermostat. The vessel was sealed to enable the operation to be carried out under vacuum conditions (mechanical pump). A vertical condenser, a safety valve and a vacuum-gauge were attached to the cover and a thermometer in a sealed metallic tube entered the reaction mixture. Sampling and final discharge of the polymeric mass were carried out by means of a 0.5 in gate valve placed at the bottom.

Oil at 95°C was circulated so that the reaction mixture attained this temperature in a few minutes, and this point was arbitrarily taken as the start of the polymerization. As the reaction proceeded aqueous and polymer phases appeared. The polymer phase was initially less dense than the aqueous one but at a certain degree of condensation inversion of relative densities occurred. After reaching an adequate conversion, temperature was increased to 130°C and the vacuum applied to give a pressure below 10 torr. These operations enabled the monomers in excess, the catalyst and water to be removed from the system.

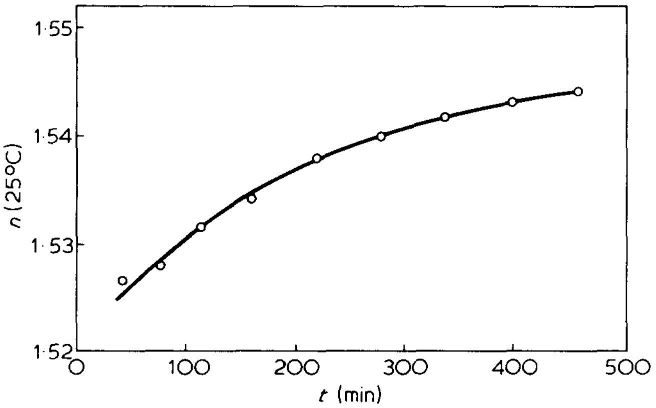

Figure 1 Increase of polymer refractive index during the reaction

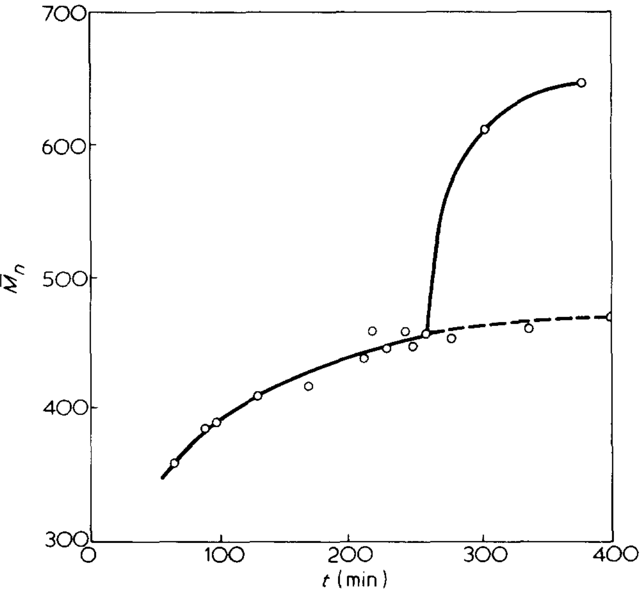

Figure 2 Increase of number average molecular weight during the reaction

Figure 1 shows the variation of the polymer phase refractive index, at 25°C, during the reaction before use of vacuum. The corresponding increase in the number average molecular weight (Fiske Osmometer G-66, benzene as solvent) is shown in *Figure 2*. The steeper change of the slope corresponds to the point where vacuum conditions are imposed (at 260 min). This is due to the removal of monomer and perhaps to some extra condensation while the catalyst was being eliminated. The final $\bar{M}_n$ was equal about to 650, being close to the tetramer value ($\bar{M}_n$ = 636). The novolac softened at 95°C but melted completely only at 177°C (Büchi SMP-20) giving a transparent liquid. The polymerization yield was 86% calculated on the basis of all the added *p*-tert-butylphenol and formaldehyde (in this case only the methylene bridge $-CH_2-$ has to be considered).

Similar functions may be used to correlate the curves plotted in *Figures 1* and *2* (before use of vacuum). Thus,

$$\bar{M}_n = A - B\exp(-k't) \quad (1)$$

$$n = C - D\exp(-k't) \quad (2)$$

with $k' = 8 \times 10^{-3}$ min^{-1}. These correlations are depicted in *Figure 3*. By using refractive index values measured

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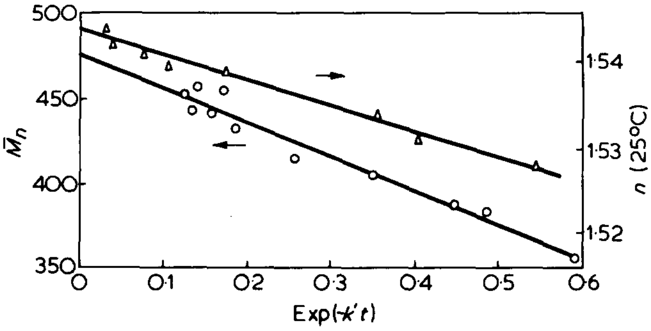

Figure 3 Correlations for the number average molecular weight and the refractive index (equations (1) and (2)

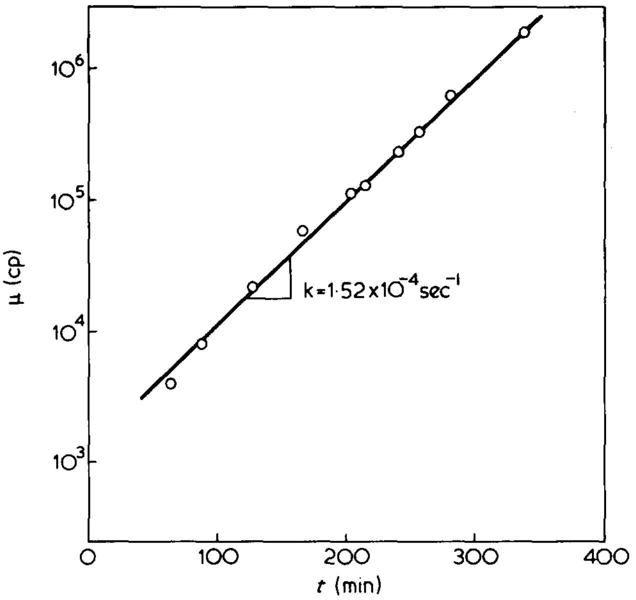

Figure 4 Polymer phase viscosity vs. reaction time, at 18°C

after 260 min of reaction without use of vacuum, corresponding values of $\bar{M}_n$ may be obtained from equations (1) and (2). These are plotted with a dotted line in *Figure 2*, showing a satisfactory extrapolation of the full curve. Equations (1) and (2) may be rewritten as:

$$(\bar{M}_n - \bar{M}_{no})/(\bar{M}_{n\infty} - \bar{M}_{no}) = 1 - \exp(-k't) \qquad (3)$$

$$(n - n_o)/(n_\infty - n_o) = 1 - \exp(-k't) \qquad (4)$$

with $\bar{M}_{no} = 276$, $\bar{M}_{n\infty} = 476$, $n_o = 1.5141$, $n_\infty = 1.5441$. The subscripts o and ∞ denote, respectively, the lower limit at $t = 0$ and the upper limit in absence of vacuum.

The fact that there is an upper limit for the number average molecular weight of phenol-formaldehyde novolacs is well established in the literature[2]. In this sense, the ratio given by the left hand-side of equation (3) may be regarded as a measure of the polymer phase conversion, implying the reaction to be fitting a first order kinetics scheme.

From equations (3) and (4) a linear relationship between $\bar{M}_n$ and n results, offering a simple possibility to follow the reaction. Thus, the appropriate point to apply vacuum may be selected from the asymptotic variation of the polymer refractive index.

The variation of the polymer phase viscosity during the reaction is plotted in *Figure 4*. Results are very well correlated with an exponential function,

$$\mu = \mu_o \exp(k_o t) \qquad (5)$$

where $\mu_o = 1260$ cp and $k_o = 2.1 \times 10^{-2}\,\text{min}^{-1}$. According to Mussatti and Macosko[3], for a linear stepwise polymerization this indicates a first order reaction. However, the overall rate constant is roughly 2.6 times higher than the one determined by number average molecular weight measurements (if viscosity had been expressed on a 10 basis, both constants would have been nearly the same). Viscosity appears to be the most sensitive parameter to follow the reaction. The relationship between μ and $\bar{M}_n$ arises from equations (3) and (5) as

$$\log\mu = \log\mu_o + 2.625 \log(\bar{M}_{n\infty} - \bar{M}_{no})/(\bar{M}_{n\infty} - M_n)$$

Intrinsic viscosity values, at 25°C, for solutions of the novolacs in benzene are shown in *Table 1*. A particular case is plotted in *Figure 5*. The following Mark–Houwink equation,

$$[\eta]\ (\text{dlg}^{-1}) = 9.33 \times 10^{-5}\bar{M}_n^{0.832}$$

provides an excellent agreement between experimental and predicted values (*Table 1*). The reduced viscosity, η_{sp}/c,

Table 1

$\bar{M}_n$	[η] (dlg^{-1}) Experimental	[η] (dlg^{-1}) Predicted	k_H	k_K
427	0.0143	0.0144	3.0	2.0
447	0.0151	0.0150	3.0	2.0
455	0.0150	0.0152	3.0	2.3
537	0.0175	0.0174	3.1	2.3
567	0.0185	0.0182	2.8	2.0
596	0.0190	0.0190	2.7	2.0
609	0.0196	0.0194	2.8	2.0
644	0.0198	0.0203	2.9	2.1

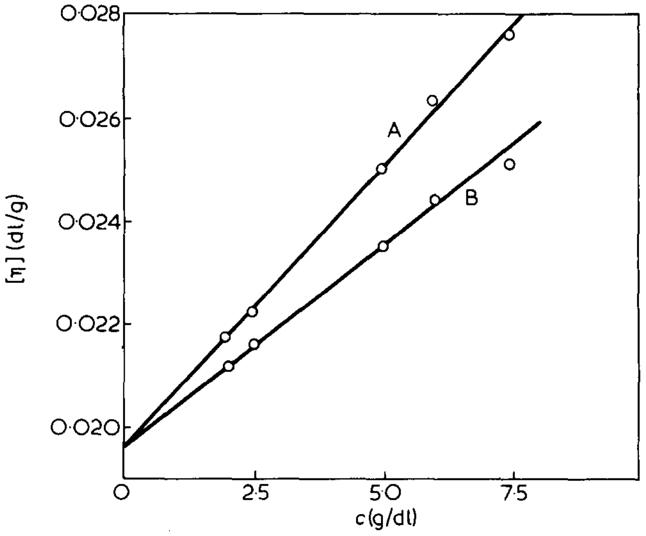

Figure 5 Reduced A (η_{sp}/c) and inherent B ($\ln\eta_r/c$) viscosities at 25°C vs. novolac ($\bar{M}_n$ = 609) concentration in benzene

follows the Huggins equation,

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c$$

with $k_H = 2.9 \pm 0.2$. Also, the inherent viscosity, $(\ln\eta_r)/c$, follows the Kraemer equation,

$$(\ln\eta_r)/c = [\eta] + k_K[\eta]^2c$$

with $k_K = 2.15 \pm 0.15$.

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Phenolic resins for oil varnishes: 2. Simple method of giving reactivity to oil-non-reactive resins

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A modified oil–resin was prepared according to the following formulation (in parts by weight): *p*-tert-butylphenol novolac ($\bar{M}_n = 650$, preparation described elsewhere[1]) = 40, tung oil = 40, polymerized linseed oil (200 poise at 20°C) = 20, hexamethylenetetramine = 0 to 6. The reactor was a one and a half litre stainless steel vessel, provided with an anchor impeller and jacketed with temperature controlled electrical heating system. A vertical condenser and a Fe–constantan thermocouple entering the reaction mixture were attached to the cover. Sampling and final discharge were carried out by means of a valve placed at the bottom.

The resin and the oil mixture were charged to the reactor and temperature was increased to a constant value (in the range 200 to 300°C) which was arbitrarily taken as the zero polymerization time (the reaction was so slow that this assumption was considered satisfactory). At this stage, the selected amount of hexa was added and the reaction taken to a point where a 1:1 wt/wt solution of the mixture in white spirit gave a viscosity of 200 to 300 cp at 20°C.

The varnish was formulated with the addition of white spirit in a weight ratio 1:1, cobalt and lead in proportions varying from 0.03%to 1% and 0.25% to 1%, respectively, with respect to total oil. These two metals were added as solutions of the corresponding octoates in white spirit.

Table 1 shows the drastic reduction in gel time resulting from the addition of hexa to the novolac, the tung oil, and their mixtures. Further, the effect on both reactants was similar, implying that a copolymerization could take place. This is important in view of the fact that when the phenolic resin acts as a mere filler of the polymerized oil, properties of the varnish film are less satisfactory[2].

The result of varying the hexa concentration is shown in *Figure 1.* A minimum in the gel time at 255°C is observed, corresponding to a hexa concentration of 5% with respect to total oil (3 parts in the formulation). At this concentration the effect of temperature was studied, giving the results plotted in *Figure 2.* At temperatures close to 300°C the gelation was almost instantaneous.

The N content of the final varnish was determined by the Kjeldahl method. It was found that the sample prepared with 5% hexa had a residual nitrogen content of only 3.3% of that added, the major part being evolved as ammonia during polymerization.

Thus, the slow process of making varnishes from oil–nonreactive novolacs may be substantially accelerated by adding suitable amounts of hexamethylenetetramine. Its effect may be visualized by returning to the observations of Hultzsch, and Cunnen, Farmer and Koch[3], supporting the presence of chromane derivatives in the reaction between

Table 1

	1	2	3	4	5
Novolac	–	100	40	–	40
Tung oil	100	–	40	–	40
Linseed oil	–	–	20	100	20
Hexa	10	15	6	10	–
Gel time at 250°C (min)	18	16	17	–	300

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