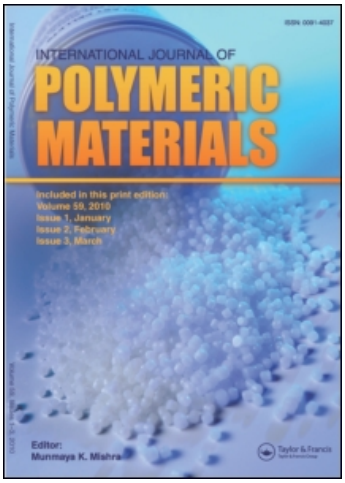

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Curing Behaviour of Poly-(1,4-phenylene sulphide) with Quinones

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The curing reaction of poly-(1,4-phenylene sulphide) (pps) with tetrachlorobenzoquinone (chloranile), quinhydrone and antraquinone are studied by X-ray diffraction differential scanning calorimetry, Fourier-transform infrared spectroscopy and thermogravimetric analysis. The results are discussed in terms of a mechanism for curing.

Keywords: Poly-(arylene sulphide); Poly-(1,4-phenylene sulphide); Curing

INTRODUCTION

Port and Still [1] suggested the important role of oxygen as hydrogen abstractor in the curing of pps. In our previous works this mechanism was confirmed in the case of curing without oxygen on the example of curing with some quinones [2, 3]. The present study was undertaken to investigate the effect of specially chosen quinones. The chosen quinones should differ in their red-ox potentials and their influence on curing should be differentiated. Then it would have confirmed curing mechanism based on intermolecular substitution [1].

EXPERIMENTAL

The curing was performed as previously [3].

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The same analytical techniques were used. Additionaly differential scanning calorimetry was done on UNIPAN DSC 605M instrument using pared aluminium crucibles. The sample size was 15 mg and the temperature was programmed to increase at a rate of 10°C/min. The Ft-IR spectra of cured samples were recorded using Bruker IFS 113f instrument.

RESULTS AND DISCUSSION

According to Brady [4] curing causes decrease of crystallinity degree. Decrease of crystallinity was observed in all samples. It decreases with the increase of additive content (Fig. 1). The lowest value is reached in the case of 20% of quinhydrone content. The least different

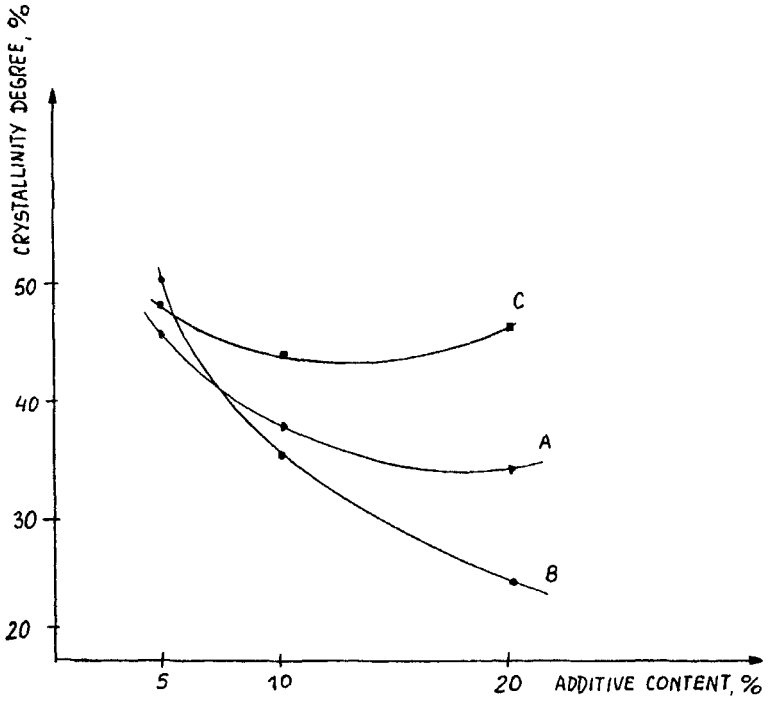


FIGURE 1 Relationship between degree of crystallinity and additive content. With A – sample cured with chloranile, B – sample cured with quinhydrone, C – sample cured with antraquinone.

from the original sample is pps cured with 20% of antraquinone content.

It was found that the melting point of cured polymer is lower than the melting point of the uncured one (Fig. 2). The lowest is the melting point of pps crosslinking with 20% of chloranile. Melting points were determined by using DSC.

The heat of fusion values are thought to coincide roughly with the melting points values. The relation between heat of fusion and additive content is shown in Figure 3.

Ft-IR spectra were done to observe expected changes in chemical structure of crosslinked polymer (Fig. 4). These spectrums were compared with the spectrum of Ryton P-3. In the spectrums of cured polymers there are 3150 and 3350 cm^{-1} bands characteristic for OH groups.

The same bands exhibits sample beated in air atmosphere prepared by N. Bulakh and coworkers [5]. If the curing had been performed in the presence of oxygen these bands could have been ascribed to phenolic structures created in the intermolecular

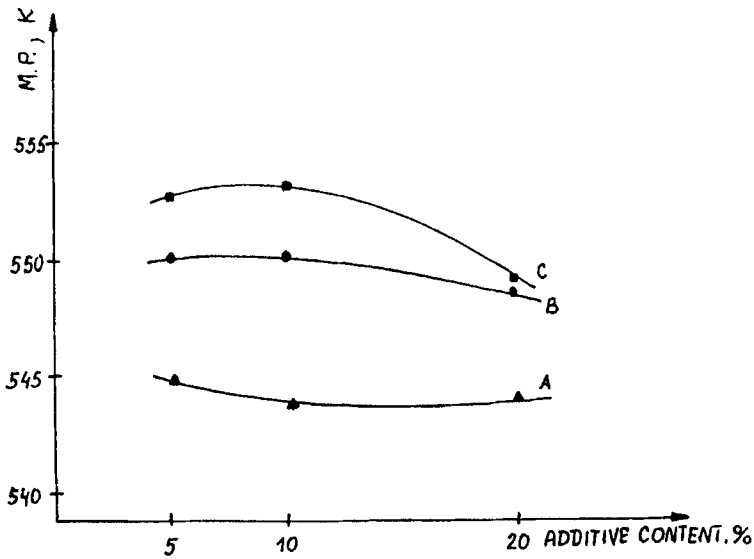


FIGURE 2 Relationship between melting point and additive content. A – sample cured with chloranile, B – sample cured with quinhydrone, C – sample cured with antraquinone.

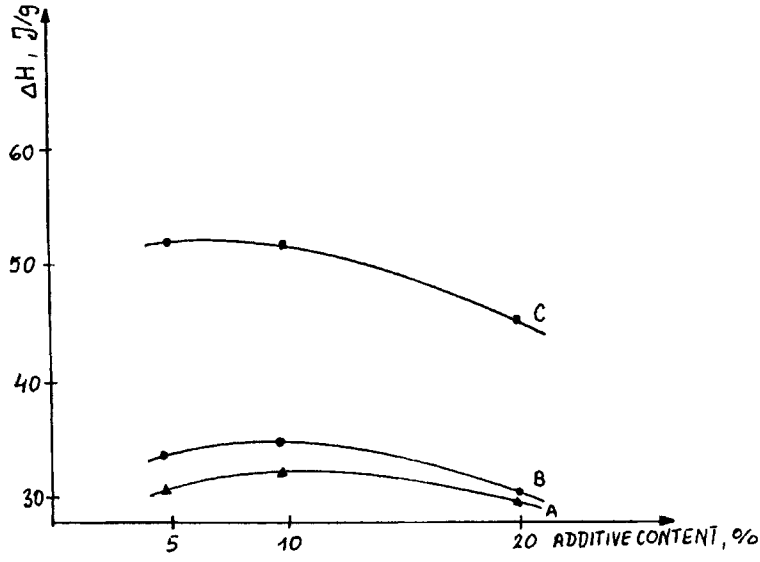
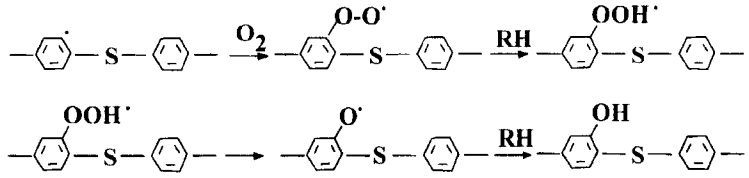


FIGURE 3 Relationship between heat of fusion and additive content. A – sample cured with chloranile, B – sample cured with quinhydrone, C – sample cured with antraquinone.

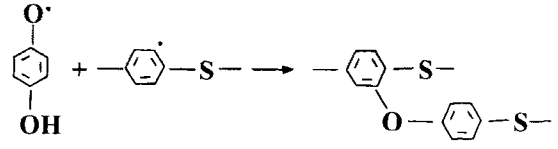
substitution (1).



(1)

However curing was performed in argon atmosphere. Hydroxy bands reflect quinone fragments built into polymer net. It must be stressed, that before making Ft-IR spectrum grinded polymer was extracted to remove quinone residues.

Although radical HOC_6H_5O is nonreactive, its reaction with S-phenyl radical cannot be excluded (2).



(2)

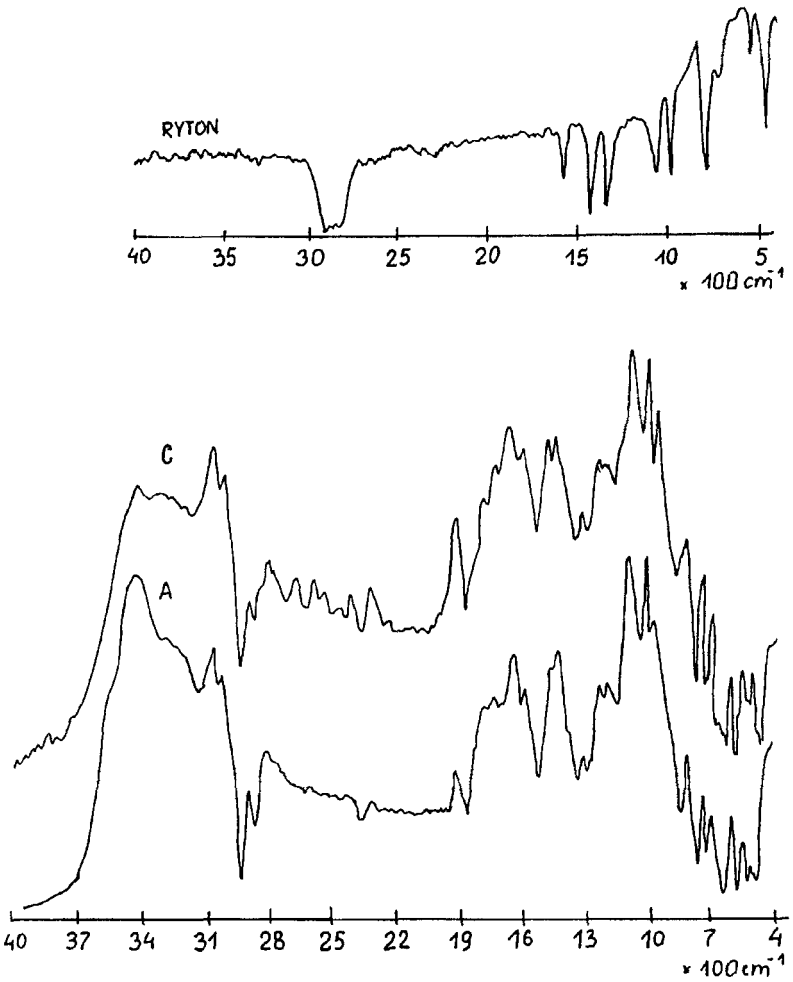


FIGURE 4 Ft-IR spectra of cured samples. A – sample cured with chloranile, C – sample cured with antraquinone.

In the range characteristic for aromatic substitution – the new band appeared at 860 cm^{-1}. It is ascribed to isolated hydrogen atom in the benzene ring (1,2,4 substitution) which is present in crosslinked chains only. The intensity of this band in greater in the sample with 20% of chloranile than in the sample with 20% of antraquinone.

For the final confirmation of curing influence of quinones TG analysis of samples containing 20% of antraquinone and 20% of chloranile was done. The samples were selected because of radically

TABLE I

Thermal stability of cured pps (TG)

*Sample**	*Temperature of decomp.°C (beginning)*	*Weight of residue, %*			*Total weight loss***, %
		400°C	450°C	500°C	
A_{20}	480	99	98	96	15
C_{20}	480	98	95	93	25
O	480	99	97	83	40

A_{20} – sample cured with 20% of chloranile.
C_{20} – sample cured with 20% of antraquinone.
O – sample cured without additives.
* Samples.
** Total weight loss corresponds to first step on TG curve.

different red-ox properties of quinones. The red-ox potential of chloranile is 0,736 V and red-ox potential of antraquinone is 0,156 V. The results were as expected, *i.e.*, admixture of chloranile causes significant increase of thermal stability greater than in the case of 1,4-benzoquinone, 1,3-benzoquinone and quinhydrone [2, 3].

This influence is much greater than the influence of antraquinone. With the admixture of chloranile the total weight loss is 15% only while in the case of antraquinone it is 25% (Tab. I).

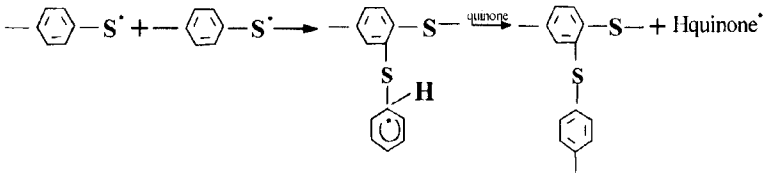
Summing up, it can be stated that chloranile strongly crosslinks pps.

Unexpectedly, antraquinone which we classified as nonreactive on the basis of red-ox potential value, proved to be active. In my opinion two effect are overlapping: nucleation effect which is promoted by high melting point of antraquinone (286°C) similar to melting point of pps. This fact may be crucial to simultaneous crystallization of polymer and antraquinone while antraquinone is the nucleating agent. It is confirmed by relatively high heat of fusion (Fig. 3) with relatively low decrease of melting point. The other effect is crosslinking as is suggested by increase of thermal stability, decrease of melting point and heat of fusion in the sample with 20% of antraquinone.

CONCLUSIONS

Heating of pps in temperature above melting point in argon atmosphere results in crosslinking.

Curing mechanism is based on intermolecular substitution (3).



(3)

This mechanism is confirmed by influence of quinones (hydrogen abstractors) on curing which is dependent on their red-ox potentials.

Acknowledgement

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